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An Investigation of the Physical Properties of Thin Films used in the Reduction of Surface Reflection *

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ABSTRACT. A simple mathematical treatment of reflection from thin films is extended to cover the properties of films likely to be met with in practice. In particular, reflection from multiple films of more than one substance is considered, and the reflection of polarized light from simple films. A photometer used for testing these results is described, and the different types of cryolite films found are enumerated.

Evidence is given suggesting that polished or aged cryolite films behave as if they consisted of a lower stratum of cryolite surmounted by a secondary layer of higher refractive index. Some of the properties of this layer are described.

§1. INTRODUCTION

THE published theoretical treatment of evaporated cryolite films used for reducing surface reflection from glass has not been extended far enough to explain observed results. A practical analysis based on the method used by Greenland (1943) has, therefore, been developed to explain the behaviour of films illuminated by polarized light, films with scattering centres within their bulk or irregularities on their surfaces, films of high dispersive power, and films consisting of layers of different refractive indices. Some of these latter conditions have now been treated by others (Mooney 1945, Vašíček 1947); the emphasis in the present paper is on a practical approach.

A simple reflection photometer was used to compare the reflectivity of actual coated surfaces with that of normal untreated glass, over eight relatively narrow bands in the visible spectrum selected by colour filters. In many instances there were departures from the performance expected from simple theory which could only be explained by a more extended treatment; in particular, measurements suggested in some cases the production, either naturally or accidentally, of a secondary layer with relatively high refractive index lying on the original simple layer, and probably penetrating some way into it. The presence of this layer was found to be of importance in producing an evaporated film which was of a stable and tough character.

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§ 2. MATHEMATICAL TREATMENT

(i) *General Method used*

In the mathematical treatment which was developed, only the condition of the reflected light was considered, as the construction of a transmission photometer of the necessary accuracy to check the behaviour of practical films was felt to be difficult. The analysis was based on the summation of multiple reflections, which shows that the intensity of light reflected depends simply on the effective reflection coefficients of the faces of a film having due regard to the path differences and transmission losses occurring within the body of the film.

(ii) *Single Films*

In the case of single films with no dispersion it can be shown that the intensity of monochromatic light I reflected from a given film varies with reciprocal wavelength or wave number $1/\lambda$, giving a curve of the form $I \simeq A + B \cos k/\lambda$ where A and B are functions of the refractive indices present in the system, with $A > B$, and k a function of the optical thickness of the film. This simplified equation, due to the linear relationship between the wave number and the phase delay introduced when a wave traverses a film of constant thickness, was found to be theoretically accurate to about 5% in practical instances.

By plotting experimental results in this way, recognizable fragments of cosine curves were usually produced from which the optical constants of the system could be deduced, although the measurements had only covered a relatively restricted waveband.

(iii) *Effect of Dispersion*

The effect of dispersion within a layer on a glass surface is two-fold: the difference in the optical thickness for different wavelengths gives a non-linear variation of phase with reciprocal wavelength and the reflecting power of the faces of the layer change with alterations of wavelength.

A possible result of this is illustrated in Figure 1. Here at some wavelength λ_2 , a reflected amplitude given by X might be observed where X is a point on the curve (i). At some other wavelength λ_1 the refractive index of the film might be higher so that a point such as Y lying on the new curve (ii) would be observed. Between λ_2 and λ_1 intermediate values would be found, so that the curve (iii) is the effective reflectivity curve of the film. The amplitude reflected could never actually exceed the amplitude reflected from a plain uncoated surface unless the film had such a high dispersion that the refractive index at some wavelength was greater than that for the glass base, but it is easy to see that incorrect maxima could be found if limited observations on curve (iii) were extrapolated without due care.

If the dispersion of the glass is to be accounted for, further modifications will be produced, but only to the reflecting power of the second surface of the layer. This would raise or lower the minima of the respective curves, but it would only alter their reciprocal wavelength values by an amount of a second order.

(iv) *Multiple Films*

It was established that in the case of single films it was unlikely that a coated surface would be produced naturally which would reflect less light than an uncoated surface at some wavelengths and more light at others. Since such conditions were frequently found the possible existence of a secondary layer of a differing refractive index lying on or within a simple layer was investigated.

It was found as a general rule that if the refractive index steps of such a multiple layer system (even of more than three interfaces) were not all of the same sign (in going, say, from air to glass), then under some conditions it was possible that more light would be reflected than if only one step of the same overall magnitude existed. If all the steps were of the same sign, then the maximum possible reflection would not exceed that from a single step of the same overall magnitude.

(v) Reflection of Polarized Light

The reflection of polarized light to be expected from thin films was also studied. It was first assumed that no birefringent effect would make itself evident, in view of the thinness of the films and the weakness of the birefringence of the materials used. As only parallel-sided films were considered, it was possible to consider any polarized incident light as made up of two quite independent components polarized in and perpendicular to the plane of incidence, for these two components would not at any time interfere with one another. These two components were therefore investigated separately.

(a) Light polarized in the plane of incidence

The interference conditions for light falling at an angle on a single coated surface are similar to those for normal incidence except that the angles of incidence, and therefore the effective reflecting properties, differ at the two faces of the film. At the same time, the optical path within the film varies with the angle of incidence of the light.

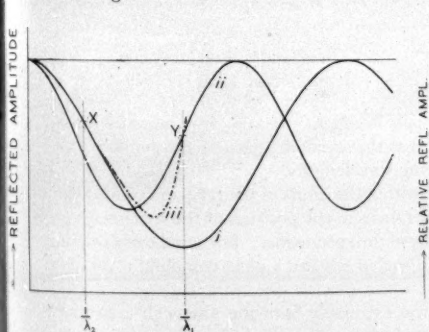


Figure 1.

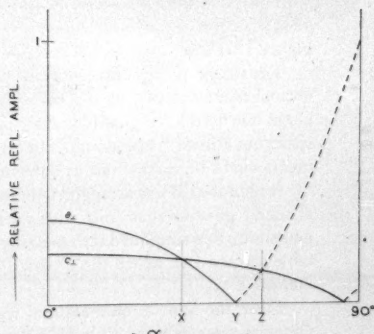


Figure 2.

For light polarized in the plane of incidence (magnetic vector) the amplitudes reflected at each face increase in a regular manner with increase of angle of incidence, but due to refraction within the film that from the upper surface will always increase at a faster rate than that from the lower face. This results in a change in the relative intensities of the interfering components and thus in a change of saturation of the interference colour produced.

(b) Light polarized perpendicular to the plane of incidence

When the light is polarized so that the magnetic vector is perpendicular to the plane of incidence, the reflection obtained at each face of the film is a more complex function of the angle of incidence and includes the Brewster condition when zero reflection is obtained. Figure 2 shows the relative amplitudes of light reflected

from the upper a_1 and the lower c_1 faces of a typical film with an index greater than the square root of the index of the glass on which it lies, a condition almost always met with in practice. These values of a_1 and c_1 are plotted as functions of α , the angle of incidence of the light on the upper face of the film. It is seen that a_1 decreases from its value at 0° to zero at Y , corresponding to the Brewster angle, then rises again but with an added phase difference of π radians. On the other hand, due to refraction within the film, c_1 decreases very much more slowly and usually only just reaches the Brewster condition when α is near 90° . The optical path through the film will increase in the same manner as for light polarized in the plane of incidence.

At X and Z , a_1 has the same value as c_1 , so that at these angles of incidence the correct interference conditions exist for the complete extinction of some wavelengths in the reflected light. Thus at either point, the reflected light should have a saturated colour.

The precise hue is determined at X by the path delay in traversing the film at the appropriate angle of refraction, while at Z the hue is determined by the path delay in traversing the film plus the additional phase retardation of π radians incurred on reflection at an angle of incidence greater than the Brewster angle.

At Y , a_1 is zero, no interference is produced and no coloration of reflected light occurs.

§ 3. PHOTOMETER

The photometer used to measure the reflecting properties of thin films deposited on glass was built almost entirely of Meccano parts; it is illustrated in Figure 3 (*a*) and its functional parts shown in Figure 3 (*b*).

The image of the lamp L was thrown on to the surface to be tested S , at nearly normal incidence (9°) by the converging lens C via a colour filter. A series of filters was used having fairly narrow pass bands distributed throughout the visible spectrum (Ilford "Spectrum" filters) so that substantially independent measurements could be carried out at differing wavelengths.

A photocell P was arranged to lie within the limits of the reflected cone of light at such a position that quite wide tolerances in the position of the specimen were possible; this simplified the changing of the specimens. For rapid test a rotating table was used on which three coated specimens and a plain comparator could be mounted.

Since the light to be measured was extremely faint the photocell used was a Cinema-Television multiplying cell, which was arranged to multiply the photocurrent emitted by the cathode by rather more than 10^4 by the process of secondary emission. A sensitive mirror galvanometer ($5 \mu\text{a}$. full-scale deflection) in the final collecting electrode circuit indicated the intensity of the light. The Cinema-Television caesioted-antimony cell surface, insensitive to infra-red, was used, since colour filters were found to be transparent to the near infra-red.

From the published data on the eight colour filters, the photocell and the light source used, it was possible to associate with each filter a wavelength of maximum transmission, which was taken as characteristic for the measurement. In spite of the difficulties introduced by the finite pass bands of the filters, much greater sensitivity was thus obtained than would have been possible with a monochromator.

The reflection from a specimen was compared with the reflection obtained under identical conditions from an uncoated surface of a similar glass block. The unwanted reflection from the second glass-air surface of each block was removed by

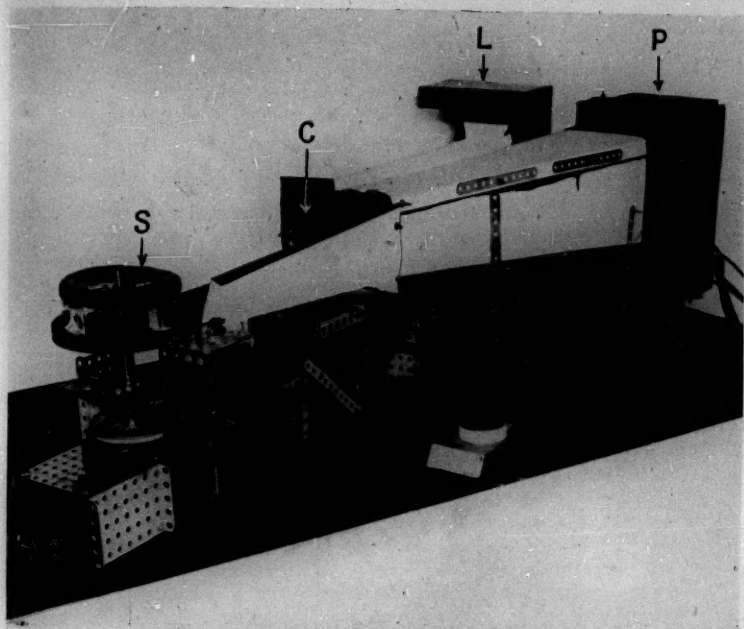


Figure 3 (a). Photometer.

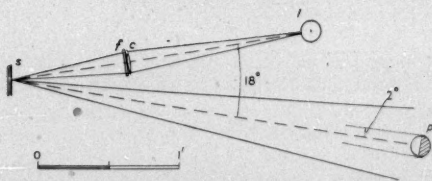


Figure 3 (b).

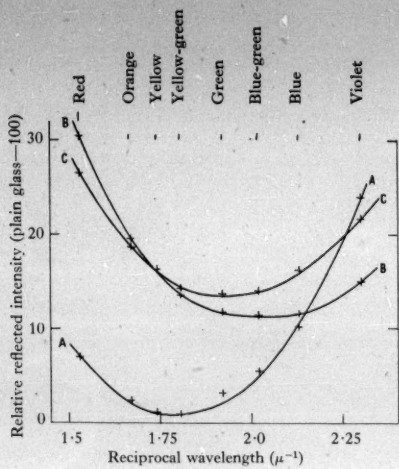


Figure 4.

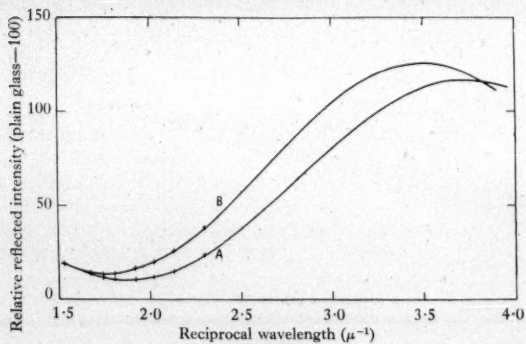


Figure 5.

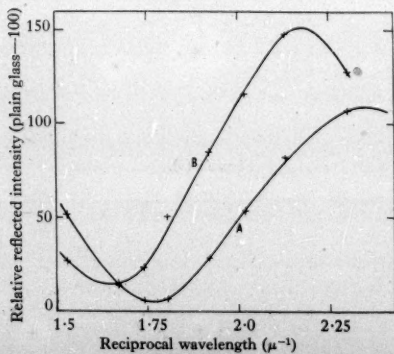


Figure 6.

placing on the back of each specimen a vaseline-charcoal paste which had a high absorption and a refractive index very near to that of glass. Measurements indicated that an absolute accuracy of rather better than 5% was obtainable and the repetitive accuracy, even over several years, was certainly much higher than this.

§4 EXPERIMENTAL RESULTS

(i) *Reflection at Near-normal Incidence*

The results given by the photometer when measurements on a large number of specimens had been made suggested the existence of several broad types of surface. Those described here were all deposited on polished glass of refractive index 1.58, unless otherwise stated, but equivalent types were found when other glass bases were used.

(a) *Low refractive index films, sometimes showing slight scattering.* These films gave the best reflectivity curves that were ever obtained. The curve of a typical specimen is given in Figure 4(A) which shows the reflectivity, expressed as a percentage of the reflectivity of a plain surface, plotted against reciprocal wavelength. By eye, the film had a fairly intense bluish-purple appearance; this is explained by the relatively high proportion of red and violet light reflected. The most interesting feature about it, however, was the extraordinarily low minimum which occurred for yellow light, as low as 1% on occasion, and in a number of cases of the order of 5%. Since 1% is the limit of observational accuracy in view of the finite pass-bands of the colour filters we may say that the range of minima met with in this class extends from zero upwards. From the minima and experiments with polarized light, it was found that the index of these films lay in the range 1.25–1.34, the latter corresponding to an 8% minimum.

Mechanically, the films were found to be very soft, and to have very poor attachment to the glass base. They were removed entirely by cotton-wool lightly rubbed over the surface. Sometimes, but not always, they showed scattered light, but since the curves were very similar to those found when no scattering was present, it was assumed that losses from this cause were small. These films seemed to be formed when the glass surface to be coated was inadequately cleaned (either chemically or electrically or both) and the pressure of the gas in the chamber at the instant of evaporation was too high.

(b) *High refractive index films, showing no scattering.* The most durable films produced were those which gave a reflectivity curve of the type shown in Figure 4(B). These had a minimum reflectivity of the order of 10–12% and as a consequence their colour, when viewed by reflected light, was never quite saturated. Calculation showed that the refractive index of these films, assumed constant, lay between 1.35 and 1.36. If the films had been solid cryolite with a refractive index of 1.364 the minimum reflectivity would have been 12.8% of that of a plain surface, and this value was not exceeded in practice when quite new films were tested. This type of film was formed only when the glass surface to be coated was quite clean and the evaporation took place at a very low pressure.

(c) *Polished films.* When films of this last type were polished with chamois-leather, reflectivity curves similar to that illustrated in Figure 4(C) were produced. Under these conditions the minimum reflectivity was always raised—the specimen illustrated was that shown unpolished in Figure 4(B)—at times to about 15%, and at the same time the wavelength at which the minimum occurred was usually increased. Both the rise in reflectivity and the displacement of the minimum

were variable factors, differing from specimen to specimen, but although in some cases little or no displacement was produced, the rise in the minimum was always found to exist, and often lay between 2% and 5%.

(ii) *Reflection of Polarized Light*

With a simple polarizing spectrometer it was possible to confirm the theoretical reflecting properties of thin films at angles of incidence other than normal. The usual prism was replaced by a specimen arranged to reflect light from the collimator down the telescope tube; the appropriate angles could then be read off in the usual way. No trace of elliptical polarization was ever detected, the observable limit being about 1%, so that it was considered that the elementary treatment was justified.

(a) *Light polarized in the plane of incidence.* When films were illuminated with light polarized in the plane of incidence (magnetic vector) the hue of the light reflected changed slowly with increasing angle of incidence as was expected from the increasing optical path within the film. The colour saturation, however, with all types of films decreased slightly with increasing angles of incidence, indicating that the index of refraction of the film was always rather higher than the square root of the glass base.

(b) *Light polarized perpendicular to the plane of incidence.* The effects observed when films were illuminated with light polarized perpendicular to the plane of incidence (magnetic vector) were also as expected. Normal films were found to show a hue which changed slightly as the angle of incidence was first increased, and which had an almost velvet-like appearance when the critical state was approached. Colour saturation occurred usually at some angle of incidence near to 40° , after which the saturation faded rapidly and the film reflected nearly white light over a large range of angles. Nearer to grazing incidence it was sometimes possible to see the approach of the second saturation condition, but this was not always obvious and was never observed at any definite point.

When some colour could be seen, however, the hue of the light reflected when the plane of polarization was in the plane of incidence was complementary to that observed when the plane of polarization was perpendicular to this, at the same angle of incidence. This was caused by the extra phase change which occurred in the latter case when the angle of incidence of the light on the air surface of the film was greater than the Brewster angle.

It was found that the angle of incidence α at which colour saturation occurred could be measured to an accuracy of about 1° , though with some films, colour filters in the eyepiece of the spectrometer were necessary to attain this figure. From these measurements the refractive index of a film could be calculated assuming only the index of the glass base. A comparison of results obtained by this method and by the photometer method described in (i) is given in two cases: for a soft film the photometer method gave minimum reflectivity 1% and refractive index 1.285 while the polarization method gave a refractive index 1.275 from a value of $\alpha = 30^\circ$; for a lightly polished film the two values were 1.367 and 1.355, from minimum reflectivity 14% and $\alpha = 46^\circ$.

In spite of the good correspondence, it was found from later work that it was not always possible to assume a simple layer of uniform refractive index in practice, so that the convenience of this single observation method was lost. In general, however, a high value of α was found to indicate a high value of refractive index.

(iii) *Effect of Polish*

(a) *General.* It was soon found in experiments on thin films that the effects of polishing were profound. The most striking observation made was that as a fresh, unpolished surface was rubbed, a characteristic squeak was produced until all the surface had been disturbed, when no amount of further rubbing, even after a period of months, would produce the squeak again. Tests indicated that the mechanical resistance to the polishing material was much higher before the squeak than after it and also that dusting or rubbing lightly with a paint-brush or cotton-wool did not cause the effect, or prevent it being found afterwards. It was found in addition that a polished surface was much more robust than an unpolished one. Thus, cotton-wool rubbed briskly over a fresh surface would partially remove it, while producing the characteristic squeak, but the remaining film, being polished, would then be very stable and resist further rubbing without even scratching.

These effects were confirmed with many polishing materials, but while silk and cotton were both found to polish without substantial initial scratching, chamois-leather was even better in this respect and was therefore more often used when photometric measurements were made.

To check these findings, a simple scleroscope was made. This instrument was not used to measure the abrasion resistance of the films, as did that due to Townsley (1945), but to produce, under carefully controlled conditions, a single scratch which could be examined microscopically. The results suggested that while on unpolished films fine continuous scratches were produced, when the same films were polished the scratching point tended to skid over the surface making a regularly spaced series of indentations into the film, doubtless due to point chatter.

These mechanical properties could have been explained by assuming that the squeak corresponded to the cleavage and pulverization of the oriented crystallites found by electron diffraction in an unpolished layer, and always absent or masked in a polished specimen (Dell, in preparation) but the optical properties produced at the same time showed that this explanation was not sufficiently detailed.

When the reflectivity results given by the photometer were extrapolated by fitting cosine curves to them, it was found that unpolished films usually gave curves which had maxima corresponding to a reflectivity of rather more than 100%. A typical result is illustrated in Figure 5, curve A, where a maximum of 116% was obtained. This value is not altogether surprising when the uncertainty of such an extended extrapolation by an approximate method is considered.

When a similar attempt was made to fit a curve to the reflectivity results obtained from the same specimen after polishing (curve B) a maximum of 126% was found. This was outside the experimental error expected, and a confirmatory check was carried out on a film (Figure 6) of such thickness that both a maximum (second order) and a minimum appeared within the visible spectrum. This particular specimen was deposited on glass of refractive index 1.61, and from the minimum of the curve found when the film was unpolished (curve A) it can be seen that the film index was about 1.34, while the maximum reflection corresponded to about 110%. As soon as the film was polished, however, the maximum rose to 150% (curve B) while the minimum shifted in the usual manner, indicating that the effect suspected in thin films certainly had a counterpart in a thick film.

In the experiments on polishing it was found that there was a great danger of contaminating the polishing surface by grease, when the polishing action tended to produce a marked bluish "smear" on a normal specimen which could only be

partially removed by brisk polishing afterwards with cotton-wool. Thin rubber sheeting wrapped round a cotton knob was found to be satisfactory except that a smear of greyish matter was deposited on the film, but this was removable by subsequent rubbing with cotton-wool. This left the film quite hard and polished to a high degree with no visible scratching. Typical reflectivity curves were found to be very similar to those produced by polishing with chamois-leather, except that the rise in the minimum reflectivity was usually rather greater, so that 16% to 17% of that of plain glass was common. The extrapolated maximum, however, was rarely greater than about 110%.

(b) *Existence of secondary layer.* It has been shown that if simple dielectrics alone are considered, reflectivity curves with maxima greater than 100% are only possible when some double layer is present in which the steps of refractive index are not all of the same sign. Thus it was likely that polishing a film produced either a zone of abnormally high refractive index at the surface or a zone of abnormally low refractive index near the glass, or possibly both these effects. Experiments were therefore carried out to determine whether such changes were present.

(c) *Special tests on polished specimens.* The experiments on hardness suggested that of the two possibilities the disturbance of the upper surface was the more probable, and from the effect of grease on the polishing material it was thought possible that grease solvents or possibly some etching technique might be found which would remove the suspected secondary layer either partially or completely; little success was obtained along these lines, but it was found that when a polished film was flooded with a solution of collodion in acetone, it was possible to strip the collodion layer off the film when it had dried out, and when this was done, some at least of the properties of the unpolished specimen were restored.

The scleroscope indicated that stripped areas of polished films were scratched exactly as new, unpolished films; zones which had been stripped stood out clearly as they reflected noticeably different and more saturated colours than the unstripped polished zones. Only in the fact that fresh polishing failed to produce any squeak did they differ from fresh specimens.

Measurements illustrating the history of a typical specimen repeatedly polished and stripped in this way are given in the table which shows the relative reflected intensity I_R and the reciprocal wavelength of the experimentally determined minima and the extrapolated maxima (the value of I_R for plain glass is 100). Curves A-G were drawn at various stages and the results obtained from them are summarized in Figure 7.

The newly deposited film gave curve A and immediately after this had been polished by the rubber process, the curve B was produced, and 36 hours later curve C. Further tests indicated that no further changes were occurring.

Three years after this the specimen was cleaned vigorously with a cotton handkerchief and curve D was plotted, and from this it seems clear that a subsidiary layer was then present. This film was then stripped (curve E), re-polished with cotton (curve F), and stripped again (curve G).

This complete cycle of changes is summarized in Figure 7 which shows the reciprocal wavelength of the minimum and the actual value of that minimum after each significant action. As can be seen, each period of polishing raised the minimum and pushed it to a smaller reciprocal wavelength, implying an increase of the total optical thickness, while each stripping lowered the minimum and

increased the reciprocal wavelength at which it occurred, implying a reduction of optical thickness.

These results were not exceptional though in a few cases it was not found easy to strip a film evenly, possibly due to faulty deposition or poor attachment to the glass, but, judged visually, the results were the same even in these cases.

Another unexpected phenomenon almost certainly of an allied nature was found in the case of fairly thick specimens which had originally been of the low index type. One of these had a maximum of almost exactly 100% when first made and a minimum of about 5%, showing that the index was then 1.32, but after 48 hours it was found that a curve of the type A in Figure 8 was produced; as is seen this had a maximum of more than 200%, the highest Figure ever found. In order to determine the crystalline state of this untouched surface, the specimen was

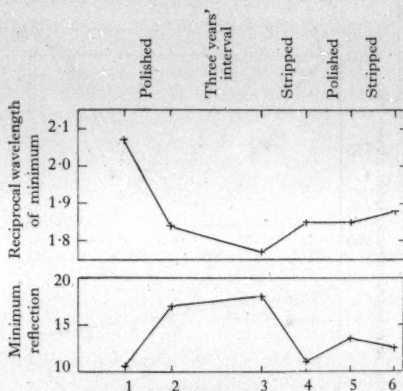


Figure 7.

Curve	Minimum (experimental)		Maximum (extrapolated)	
	I_R	μ^{-1}	I_R	μ^{-1}
A	10.6	2.07	115	4.14
B	17	1.84	114	3.68
C	16	1.85	—	—
D	18	1.77	128	3.54
E	11	1.85	109	3.7
F	13.5	1.85	119.5	3.7
G	12.5	1.88	112.5	3.76

placed in an electron diffraction camera, but under the influence of the vacuum conditions or of the low velocity (150 v.) subsidiary electron stream, the surface "peeled" quite suddenly, forming a fine silvery dust of curled flakes of film lying on the glass. When these were dusted off with a brush, it was found that a portion of the film remained behind, leaving a perfectly even pale brownish-coloured layer, which gave the reflectivity curve B in Figure 8.

Little can be deduced from this latter curve, but it is possible that it represents the lower portion of the multiple film whose existence was implied by curve A and which might have remained after the sudden removal of the upper component.

The only other specimen which stripped itself in this way did not leave a surface suitable for photometric work, but judged by eye it was rather thicker than the one illustrated.

(d) *Inferences.*

Probable nature of layer. All these experiments indicated that it was quite likely that the changes found in evaporated films when they were polished or allowed to age could be explained if it were assumed that both these processes tended to produce on the free surface of the films secondary layers of a relatively high refractive index. From the restricted range of wavelengths observed by the photometer it was difficult to gain much information about the optical properties of the secondary layer and it was even uncertain whether it lay on or within the boundaries of the original film, but some suggestions may be made as to its probable properties.

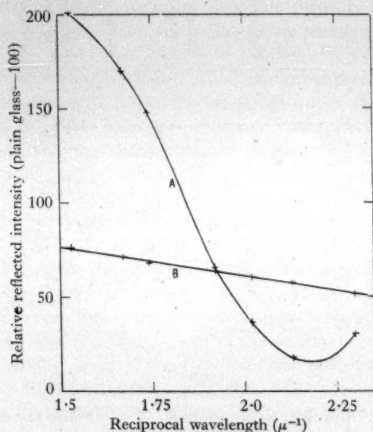


Figure 8.

In Figure 6 (B) a maximum reflectivity of 150% is shown; the minimum refractive index of the subsidiary layer necessary to produce this reflectivity can be found from the theoretical analysis. If it is assumed that the refractive index of the cryolite was 1.34, even after polishing, and that the phase relationships were such as to produce reinforcement by all components at the wavelength of maximum reflection, then it can be shown that the refractive index of the extra layer must be 1.4. If, as is probable, the phase relationships were not so favourable, a higher index would be necessary. Similarly, in Figure 8 (A) the maximum of about 200% indicates an index of at least 1.43 for the extra layer, if such a single extra layer exists.

Assuming that such layers were possible, it was necessary to find whether the curves as a whole were of the form that might be produced by such means. Theoretical curves were therefore drawn showing the effect on the reflectivity

curve when different thicknesses of material of a relatively high refractive index lay on the surface of a normal film. In Figure 9 are shown approximate curves which give the general trend of the results, and agree with the exact formula to an accuracy of better than 5%.

In Figure 9 it is assumed that a film of cryolite of 0.1μ thickness and refractive

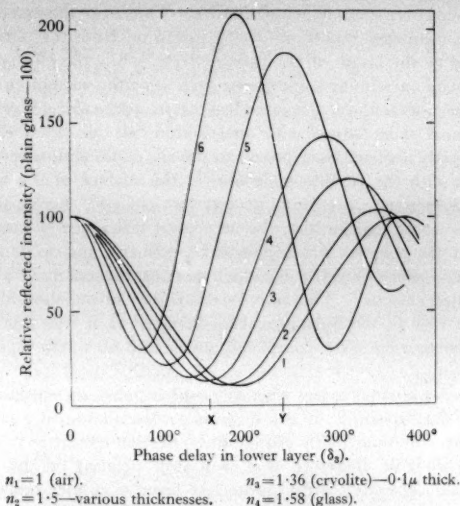


Figure 9.

index 1.36 lying on glass of refractive index 1.58 is covered by a layer of material of index 1.5. Reflectivity curves are plotted as a function of phase for thicknesses of the subsidiary layer between 0 and about 0.1μ . The portions of these curves which would be observed by the photometer lie between the points X and Y on the phase scale. For other thicknesses sections of the curves observed would lie at other points along the phase axis, scaling the actual thickness of both layers in the same manner.

It can be seen from these curves that the rise in the maximum and minimum and the change in their positions as the subsidiary layer increases in thickness are all of the order of magnitude that were found in practice; in particular, the extreme sensitivity of the reflectivity curve is shown when even as little as 50 A. of any extra material is added to a surface.

An experimental fact not yet satisfactorily explained is that often when polishing was carried out (Figure 5) the shift in the minimum found was less and the rise in the minimum more than would be indicated by a simple process such as has been visualized here. While this explanation might be partly right, therefore, it does not entirely cover the facts. On the other hand, the marked departure of the curves shown in Figure 9 from a simple cosine law explains the rather low values

that were sometimes found for the maximum reflectivity of polished specimens when these were calculated by extrapolation assuming such a simple law.

Possible causes of layer. It is not difficult to imagine how such additional layers could come to lie on the surface of the cryolite, for many animal and vegetable fats and oils have refractive indices between 1.47 and 1.48, and the manner in which such oils can creep over surfaces is well known. Thus even the vaseline ($n = 1.49$) used to reduce unwanted reflection, or the pump oil from the diffusion pumps ($n = 1.48$) could be the origin of the ageing effects, while the effects of polishing might well depend on rubbing some grease such as cotton seed oil ($n = 1.475$) into the upper layers of a film. Chamois-leather in particular (Woodroffe 1941) consists of animal skins tanned with unsaturated fish oils ($n = 1.48$) and these, though often partly oxidized by exposure to the air, could almost certainly form a very close link with the cryolite molecules in the surface of the film, giving a particularly stable layer.

These facts would explain, too, the very great difference in mechanical properties between the polished and unpolished specimens, and no doubt a smooth, grease-protected surface would be in a much more permanent and stable state than newly evaporated cryolite. This improved stability of polished films was very marked in the case of moisture-provoked changes, as it was found that well-polished specimens were often completely unaffected by water vapour from any source.

It is not at once obvious in just what way rubber polishing operates but there is no doubt that the deposition of any form of contamination of a relatively high refractive index would inevitably change the reflection conditions in the manner shown. It is probable, therefore, that even after cleaning off the grey smudge produced by such polishing, a thin protective layer of rubber remained behind. Too few experiments have been made on rubber-polished films to obtain much information about them, but doubtless the effect was similar in nature if not in detail to polishing with other materials.

It was found necessary to assume that in many cases the additional layer had an appreciable thickness and it is strange that even layers of the order of 250 Å. or more were so well-attached to the cryolite that repeated heavy rubbing with other polishing agents did not always change them. The self-stripped specimens suggest, however, that the high-index layer may sometimes penetrate some distance into the original cryolite film, since this would explain the rupture of the specimens under the action of the discharger, a known degreasing process. It is just possible that oil or grease could soak into the upper regions of a film, probably increasing the mechanical dimensions as it did so, but making a relatively strong mass rather than a weak layer of mobile oil on a hard surface.

In addition to this, if such soaking existed it is probable that the simple condition suggested of two films each of uniform optical density would rarely occur in practice. It would be far more likely that the different materials would merge into each other so that more complicated conditions of reflection would exist. These would probably explain the difficulties that have been found, but their theoretical treatment is not simple.

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An Extended Theory of the Reflection Echelon Grating

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ABSTRACT. The single reflection echelon grating has the disadvantage that it is impossible to interpret the fringe pattern without further information about the correct order allocation. The present methods of obtaining this information are briefly reviewed; they are progressively less useful as the wavelength decreases into the ultra-violet. The properties of the grating are investigated theoretically when the light is incident at relatively large angles in two special cases, and the performance of the instrument in these positions compared with that of its normal use. It is shown that the required order allocation could be obtained using a single reflection echelon grating by measuring the fractional order separation with the grating in two positions. This would considerably increase the value of the instrument.

§ 1. INTRODUCTION

THE importance of the reflection echelon grating in the field of high resolution spectroscopy is due partly to the fact that it has a good uniform performance over a wide range of wavelength. But, more especially, it can be used for the determination of absolute wavelengths and of small wavelength differences in the ultra-violet where all other high resolution instruments cannot be used for various reasons. The only exception to this is the vacuum concave grating whose resolving power is inferior to that of the other instruments.

However, when the reflection echelon grating is used in the ordinary manner with crossed auxiliary dispersion, it is impossible to interpret unambiguously the fringe pattern, i.e. to give the fringes their correct order numbers, the order of a fringe being the integral number of wavelengths in the optical path difference of two consecutive interfering rays. Also it is impossible to detect the coincidence of the fringe systems of different components when this occurs. Thus until additional information is obtained, the true character of the spectral complex under consideration cannot be deduced.

It is proposed here to extend the theory of the reflection echelon grating and to show how, using one such instrument, it would be possible to make suitable observations which allow the correct interpretation of the fringe system to be made.

§2. REVIEW OF THE PRESENT METHODS OF FRINGE INTERPRETATION

We show in Figure 1 the type of intensity distribution we should get with a simple spectral complex consisting of two components of unequal intensity. The intensity envelopes are shown for reference. The most general order and wavelength allocations are given below the diagram.

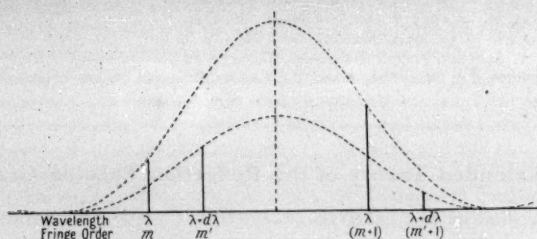


Figure 1. Intensity distribution for a two component complex.

The fractional order separation of the fringe of order m' of the component $(\lambda + d\lambda)$ from the fringe of order m of the component λ is given by $f = x/y$, where x is the mean separation of two adjacent fringes of different components, and y that of two fringes of the same component.

If we use the fact that the product of the order and wavelength is a constant for any one angular position, we get the following relation

$$d\lambda = (m - m' + f)\lambda/m. \quad \dots\dots(1)$$

The one plate alone gives no information about the value of $(m - m')$, and $d\lambda$ is one of several possible values; $(m - m')$ will be referred to as the overlapping.

The information needed to resolve this uncertainty may be obtained by two essentially different methods.

Probably the more convenient method is to use another high resolution interferometer whose fringes are of considerably different order of interference. If the fractional order separation is measured, the correct order of the overlapping is easily deduced. The instrument may be used separately or combined with the reflection echelon grating and its performance need not be as good. However, the limitations of the various interferometers restrict the use of this method to wavelengths greater than 2000 Å. We shall not consider the use of a second reflection echelon grating, as few laboratories have two such instruments available and we wish to investigate the methods of analysis which use only one of these instruments.

Alternatively the reflection echelon grating and the auxiliary dispersive apparatus may be mounted so that their dispersions are parallel. They may then be set so that their dispersions are assisting or in opposition and there is a small change in the fractional order separation in the two positions. This shift can be used to deduce the value of the overlapping. The shift in the ultra-violet using a quartz spectrometer is easily detected; Williams (1948) observed a shift of some 4% in the near ultra-violet using an E1 spectrometer. But the lower wavelength limit of use of a quartz spectrometer is in the region of 2000 Å; for shorter wavelengths a diffraction grating must be used. There is no recorded instance of its

use up to the present time, but a simple calculation gives the following formula for the change in fractional order separation in the two positions using a concave grating in the Eagle mounting :

$$\Delta f = \{Mns/[1 - (Mn\lambda/2)^2]^{1/2}\}(m - m' + f)\lambda/t,$$

where M is the order of the concave grating in which observations are made, n the number of lines per centimetre of the grating, s the offset of the echelon grating, and t the echelon plate thickness. The substitution of typical values indicates that the method would be unreliable for wavelengths shorter than 1750 Å.

The parallel type of mounting, moreover, has the general defect that it can be used only when the number of spectral lines present is small and they are well spaced. Thus the method is applicable in a strictly limited number of cases.

Hence it would appear that while the present methods of employing a single reflection echelon grating are satisfactory in the visible and near ultra-violet spectral regions, they become progressively less useful as the wavelength decreases. We are therefore led to investigate the possibility of using a single reflection echelon grating in a suitable manner which would enable the correct order allocation to be made, and the true nature of the spectral complex derived.

§ 3. THEORY OF THE REFLECTION ECHELON GRATING

The reflection echelon grating is usually mounted so that the light is incident almost perpendicularly upon the plate offset, the incident and diffracted beams making small angles with the normal. We now wish to investigate its properties when the light is incident from two other directions. For convenience of description we shall refer the grating to rectilinear axes, the yz plane being parallel to the plate offsets with the z direction parallel to their long edges; the x direction is thus that of the offset normal. Then, in the usual mounting, the light is incident in the xy plane and makes a small angle with the x direction.

(i) Light Incident almost in the xz Plane and at Large Angles of Incidence

The general directions of the incident and diffracted beams are shown in Figure 2. The angles α and β are the angles made by the incident and diffracted

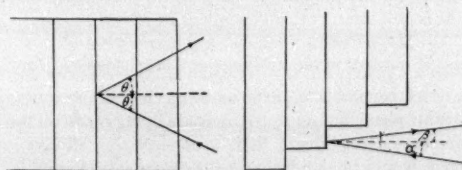


Figure 2.

(a) Section in the xz plane.

(b) Section in the xy plane. (Rays not in the plane.)

rays respectively with the xz plane and are positive when on the same side of the normal. From the geometry of the figure the path difference between corresponding rays at adjacent offsets is $2t \cos \theta (\cos \alpha + \cos \beta) - s (\sin \alpha + \sin \beta)$.

The general expression for the total intensity distribution from N regularly spaced offsets is $I = I_s (\sin N\phi / \sin \phi)^2$, where 2ϕ is the phase difference between corresponding rays and I_s represents the intensity distribution from one offset.

The intensity distribution of the light diffracted from one offset is given by the expression $I_s = I_0(\sin \psi/\psi)^2$ where $\psi = \pi(\sin \alpha + \sin \beta)s/\lambda$ and I_0 is a constant.

Thus in this case, we have $I = I_0(\sin \psi/\psi)^2(\sin N\phi/\sin \phi)^2$ where

$$2\phi = 2\pi\{2t(\cos \alpha + \cos \beta) \cos \theta - s(\sin \alpha + \sin \beta)\}/\lambda.$$

In practice, the angles α and β will be very small so that the usual trigonometrical approximations ($\sin \alpha = \alpha$, etc.) can be applied safely. Hence for the principal maxima $2t \cos \theta - s(\alpha + \beta) = m\lambda$ or defining an angle Δ by $\Delta = \alpha + \beta$, we get $2t \cos \theta - s\Delta = m\lambda$; Δ represents the angular displacement from the rays obeying the laws of reflection.

The following formulae for the grating are easily obtained by differentiating this expression and using the approximate relation $2t \cos \theta = m\lambda$ where appropriate:

Dispersion: variation of Δ with λ at constant order number $\partial\Delta/\partial\lambda = 2t \cos \theta/s\lambda$.

Dispersion of orders: variation of Δ with order of interference for one wavelength $\partial\Delta/\partial m = \lambda/s$.

Wavelength range ($\Delta'\lambda$) between successive orders: $(\Delta'\lambda) = \lambda^2/2t \cos \theta$. This is the maximum wavelength difference possible between two components so that no overlapping occurs.

Resolving power: $\lambda/\delta\lambda = Nm = 2Nt \cos \theta/\lambda$, where $\delta\lambda$ is the smallest wavelength separation measurable at a wavelength λ .

These formulae are very similar to those of normal incidence which are

Dispersion $\partial\Delta/\partial\lambda = 2t/s\lambda$ Wavelength separation $(\Delta'\lambda) = \lambda^2/2t$
Dispersion of orders $\partial\Delta/\partial m = \lambda/s$ Resolving power $\lambda/\delta\lambda = 2Nt/\lambda$.

The graph of Figure 3 shows the variation of the performance of the reflection echelon grating with the angle θ . In each case the corresponding value at normal incidence has been taken as being unity. The broken line gives the variation of a quantity which we shall call the fractional change in path difference. This is given by $(L - L')/L$, where L is the path difference at normal incidence and L' that under the given conditions.

It will be seen from the graph that there is a relatively small deterioration in the performance of the instrument. One point of particular interest is that the dispersion $\partial\Delta/\partial\lambda$ is still linear, i.e. independent of Δ .

(ii) *Light Incident in the xy Plane at Large Angles of Incidence*

This is really the general case of the usual method of mounting as the light is incident in the same plane, but no restrictions are being made on the magnitude of the angle of incidence except that it shall be so large that all rays incident on the offset, if reflected, would be incident upon the plate side (Figure 4). Expressed symbolically, this is $\tan^{-1}\theta > s/t$ where s and t are the plate offset and thickness respectively.

Considering any two corresponding rays at adjacent offsets, it is easily shown that the path difference between them is given by $t(\cos \theta + \cos \epsilon) - s(\sin \theta + \sin \epsilon)$ and is independent of the intermediate angle of diffraction γ .

The resultant intensity of illumination in the focal plane of the collecting lens in the direction ϵ , is given as before by

$$I = I_s(\sin N\phi/\sin \phi)^2,$$

where

$$2\phi = 2\pi\{t(\cos \theta + \cos \epsilon) - s(\sin \theta + \sin \epsilon)\}/\lambda.$$

The intensity distribution I_s from the single element is not so easily found exactly as in the case of the long reflecting strip. However, an elementary consideration of the physical principles involved indicates that the distribution will be similar to that of a reflecting strip of width $2s$, the light being incident at an angle θ and diffracted at an angle ϵ . The actual shape of the intensity envelope is of little importance provided there are no unusual singularities present and that the angular separation of the central minima is sufficient to contain two orders of each component.

Thus the intensity will be given by $I = I_0(\sin \psi/\psi)^2(\sin N\phi/\sin \phi)^2$ where $\psi = 2\pi(\sin \theta - \sin \epsilon)s/\lambda$. For the principal maxima of the diffraction pattern, we have $t(\cos \theta + \cos \epsilon) - s(\sin \theta + \sin \epsilon) = m\lambda$.

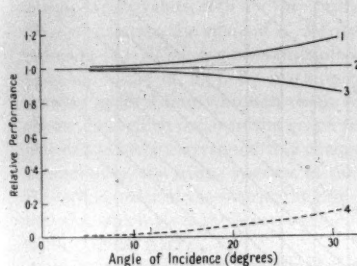


Figure 3. Variation of the relative performance with the angle of incidence.

1. Wavelength separation of orders Δ/λ .
2. Dispersion of orders $\partial\Delta/\partial m$.
3. Resolving power and dispersion $\partial\Delta/\partial\lambda$.
4. Fractional change in path difference.

If we define an angle Δ through the relation $\Delta = \epsilon - \theta$, a consideration of the magnitudes involved shows that we may write $\sin \epsilon = \sin (\theta + \Delta) = \sin \theta + \Delta \cos \theta$ etc. where Δ represents the angular displacement from rays obeying the normal laws of reflection. Then for the principal maxima we have

$$2(t \cos \theta - s \sin \theta) - \Delta(t \sin \theta + s \cos \theta) = m\lambda.$$

The following formulae for the reflection echelon grating are easily obtained by differentiating this equation and using the approximate relation

$$m\lambda = 2(t \cos \theta - s \sin \theta)$$

where appropriate:

Dispersion, i.e. at constant order number:

$$\partial\Delta/\partial\lambda = 2(t \cos \theta - s \sin \theta)/\lambda(t \cos \theta + s \sin \theta).$$

Dispersion of orders: $\partial\Delta/\partial m = \lambda/(t \sin \theta + s \cos \theta)$.

Wavelength range between successive orders: $\Delta\lambda = \lambda^2/2(t \cos \theta - s \sin \theta)$.

Resolving power: $\lambda/\delta\lambda = Nm = 2N(t \cos \theta - s \sin \theta)/\lambda$.

The performance of the instrument is shown in Figure 5. As in the previous case the broken line gives the variation of the fractional change in path. The value 10 has been assumed for the ratio of plate thickness to plate offset. However, it is only a relatively unimportant factor and the curve will be very similar for any other

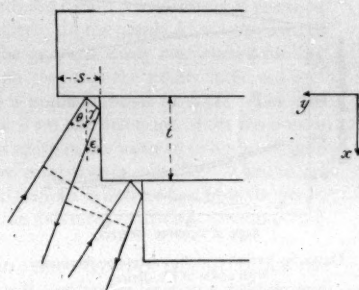


Figure 4. Section of the echelon grating in the xy plane.

value of the ratio. The graph indicates clearly that while there is no great deterioration in the resolving power, the dispersion falls away very rapidly. This is likely to be a very serious defect in view of the small dispersion of the instrument even in its usual mounting.

§ 4. USE OF A SINGLE REFLECTION ECHELON GRATING FOR ORDER ALLOCATION

Without considering at this point the relative merits of the two possible methods of use investigated, we shall see how it would be possible to use either of them to decide the question of the correction order allocation.

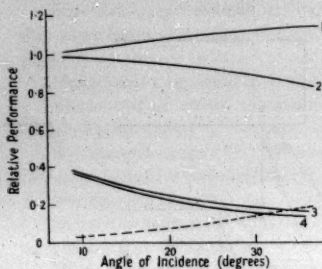


Figure 5. Variation of the relative performance with angle of incidence.

1. Wavelength separation of orders ($d'\lambda$).
2. Resolving power.
3. Dispersion of orders $\partial\Delta/\partial m$.
4. Dispersion $\partial\Delta/\partial\lambda$.

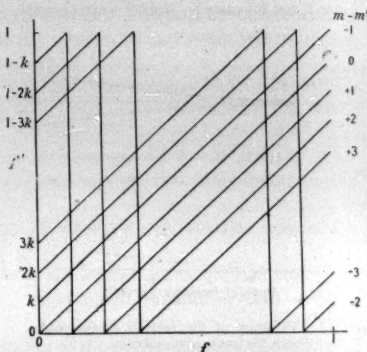


Figure 6. Graph showing the relation between the measured fractions in the two positions.

The reflection echelon grating is first used in the normal mounting and accurate measurements are made on the various fringe separations. Then when the question of the order allocation is decided, the wavelength distribution and separations of the components can be derived.

The essence of the method proposed is to alter the path difference between rays from adjacent offsets by having the light incident from one of the two directions previously investigated, and then from the new fringe separations we can deduce the correct order allocation.

Considering a fringe distribution similar to that of Figure 1, and giving the same general order allocation, the measured fraction is related to the component wavelength separation by the expression

$$d\lambda = (m - m' + f)\lambda/m, \quad \dots\dots(2)$$

as previously given. Now m , the order of interference, is connected with the path difference between corresponding rays by the relation $m\lambda = L$, and thus equation (2) becomes

$$d\lambda = (m - m' + f)\lambda^2/L. \quad \dots\dots(3)$$

Now supposing that we use the echelon grating in such a manner that the path difference is altered to some smaller value L' . This will cause a change in the fringe pattern and the new measured fraction f' will be given by

$$d\lambda = (n - n' + f')\lambda^2/L', \quad \dots\dots(4)$$

where the n 's are the new orders of interference of the two components.

We shall consider the measured fraction between two components in the various echelon positions to be that between a fringe of one component, for instance the component which we designated $(\lambda + d\lambda)$, and the nearest fringe of the other component on the *shorter path difference side*. This is by no means the only way in which we can define the fractional order separation and, in fact, the actual definition adopted is of little consequence provided the same method is always used.

Then from equations (3) and (4), we get

$$f' = (m - m')L'/L - (n - n') + fL'/L. \quad \dots\dots(5)$$

The relation between the two measured fractions given by equation (5) is best shown graphically by plotting f' against f for various values of $(m - m')$. The corresponding values of $(n - n')$ are easily deduced from a consideration of equation (5) as we decrease the value of L'/L from unity. In the graph, k has been used to represent $(L - L')/L$ for convenience. The graph is easily constructed for any particular value of L'/L by marking off on the axes the points indicated and drawing parallel lines through them with a gradient equal to L'/L . The discontinuities which occur in the graph result from our definition of the fraction to be measured and correspond to a change of unity in the value of $(n - n')$. At the discontinuity, the fringe systems of the two components coincide. Thus to get the correct order of the overlapping $(m - m')$, we have only to find from the graph the value which gives the correct value for the measured fraction f' corresponding to the original fraction f .

If the components are nearly of the same intensity, it is quite likely that the fraction measured in the second position will not be the fraction satisfying our definition but that given by $f'' = 1 - f'$. This, in practice, will lead to little trouble, if any, as we shall find that there is no fraction of this value on the graph corresponding to the original fraction and thus we should naturally try the fraction given by $(1 - f')$.

The fractional separation of two different values of the overlapping in the second position is equal to $(L - L')/L$ so that if we can measure the fraction to an accuracy of about one quarter of this amount, we can always derive the correct order of overlapping. Thus if we can measure a fraction to one hundredth of an order, the fractional change in path difference can be made equal to a twentieth or so. A value of a tenth would probably be very convenient as a fixed position in which the second fraction is to be measured.

In the rarer case when we have the coincidence of the fringe patterns of two different components in the original position, this will be at once obvious in the second position by the appearance of another pair of fringes. The large fractional separations of different values of the overlapping ensures that the components will now be clearly resolved.

§ 5. DISCUSSION OF THE PROPOSED METHODS OF USE

Any method of using the reflection echelon grating so that the path difference of corresponding rays is different in the two positions will be theoretically suitable for the allocation of order numbers. The position in which the fringe measurements must be made with high accuracy will be that in which the grating is used in the normal manner and the graphs of Figures 3 and 5 show clearly that this is the position of optimum performance. In the second position, no great accuracy is required: if the fractional change in path difference is equal to a tenth, the

fractional fringe separation need only be measured to one-fortieth of an order. Therefore, a relatively large deterioration in the performance of the instrument is permissible.

The first method of having reflections from the offset and from the plate edge has the advantage that the diffracted beam returns along the path of the incident light so that the instrumental set-up can be very similar to that normally used, the only modification needed is some arrangement for tilting the echelon grating through the required angle. But the disadvantages are so great that this method will probably not be practicable. It is highly improbable that the plate edges are polished to the high standard required and adjusted perpendicularly to the plate offset and the cost of so doing would be very great. At the same time, the dispersion falls away very rapidly with the increase in the value of the fractional change in path difference, and in view of the small angular dispersion of orders of the instrument even in its most favourable position this becomes a prohibitive factor to the use of this mounting, especially as it is most likely to be needed in the ultra-violet where the dispersion is least.

The second method appears to be much more promising. The performance of the instrument remains very good and the small decrease in dispersion is quite tolerable. Further, the performance depends only on the surface finish and accuracy of the plate offsets and this must be good for the normal use. The great disadvantage is that the diffracted light does not return along the direction of the incident light and thus the ordinary type of mounting cannot be used. There appears to be no practicable arrangement of mirrors which will reflect the diffracted beam along the direction of the incident beam. The grating would probably have to be mounted in a manner similar to that of the plane diffraction grating. This is unfortunate in that it involves another lens and a complete rearrangement of the auxiliary dispersive apparatus, yet as we can tolerate some deterioration in performance, the quality and adjustment of this apparatus need not be as good as that of the principal apparatus.

§ 6. CONCLUSION

The theoretical investigation of the properties of the reflection echelon grating shows that the performance remains relatively good as the angle of incidence in the plane parallel to the plate edges is increased. Measurements on the fringe patterns at two angles of incidence will be sufficient to enable the true nature of any close spectral complex to be deduced. The method will be applicable throughout the range of the instrument which will need no additional constructional accuracy. The disadvantage of the method is that the auxiliary dispersive apparatus would need to be rearranged.

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The Duality between Interlinked Electric and Magnetic Circuits and the Formation of Transformer Equivalent Circuits

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ABSTRACT. When making calculations on a circuit, containing both electric impedances and transformers, it is frequently desirable to consider the transformers removed and the constraints they impose replaced by a rearrangement of the impedances connected to their terminals. Such "equivalent circuits" may not always be found; the rules are here established for their formation, and also for checking, by inspection, whether the transformer constraints are removable in this way, in any particular case. It is shown that the equivalent electric circuit of a transformer, having any arrangement of magnetic paths, is derivable from its magnetic circuit by application of the topological principle of duality. This cannot be done if the magnetic circuit is non-planar, as in the case of a transformer possessing four or more windings with leakage couplings; a physically realizable circuit does not then exist.

Under certain conditions the principle may be applied in reverse and the impedances in a given electric circuit may be coupled together by a suitable transformer, so that the various current and voltage constraints are unaltered.

§ 1. INTRODUCTION

THE simple geometrical relation which exists between inverse, or *dual*, circuits (Russell 1904) of electric impedances, based on the interchange of junction-points and meshes, is well known, and has been shown by Cauer (1934) to be based on the topological principle of duality. It is intended in this paper to show that an identical relation of pattern exists between the magnetic circuit of a transformer and its "equivalent electric circuit". Furthermore, there exists a simple inverse relationship between the magnetic impedances of the transformer and the electric impedances in the equivalent circuit, in a manner analogous to the impedance relations in the inverse *electric* circuits referred to above. By way of illustration, figure 1 shows such a pair of electric inverse (or dual) circuits. Given the first circuit A, a point is marked inside every mesh $a, b, \dots$ and one external to the circuit k ; these points, when joined together as shown by the dotted branch lines, form the junction points of the dual circuit pattern B. This dual circuit B now has impedances inserted in its branches $Z_1, Z_2, Z_3, \dots$ which are proportional to the admittances $a_1, a_2, a_3, \dots$ in corresponding (crossing) branches of the first circuit A, in the sense $Z_1 : Z_2 : Z_3 : \dots = a_1 : a_2 : a_3 : \dots$ or $Z_a = K^2 a_a$, where K is any real constant. This network transformation replaces mesh connections in one circuit by star-point connections in the other and vice versa. The element *kinds* must also be changed, thus: capacity C in 1st circuit is replaced by inductance L in 2nd circuit and vice versa; resistance R is replaced by conductance G and vice versa. Corresponding impedance magnitudes in such a pair of circuits are thus reciprocally related. This type of dual relationship is reversible, and starting with a circuit such as B the dual circuit A would be

derivable. Using the symbol $\rightleftharpoons$ to mean "is dual to", the relationships between such a pair of circuits may be summarized thus :

$$L \rightleftharpoons C; \quad R \rightleftharpoons G. \quad \dots\dots(1)$$

Again it will be found that voltages across branches in one circuit $v_1, v_2, \dots$ are proportional to the currents in corresponding (crossing) branches of the other, dual, circuit, so that

$$v \rightleftharpoons i. \quad \dots\dots(2)$$

If one of the circuits forms a non-planar figure (so that it cannot be drawn on a flat sheet of paper without any one branch crossing another) there exists no dual circuit, except by the use of a special artifice given by Bloch (1946).

Analogous relationships will now be established for transformers and their equivalent circuits, taking for granted the rules for the setting up of dual mesh and branch patterns illustrated by Figure 1, and without employing the specialized notation and language of topology.

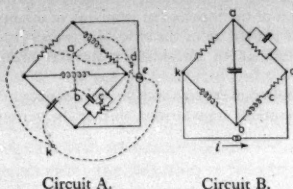


Figure 1. Method of constructing dual circuits.

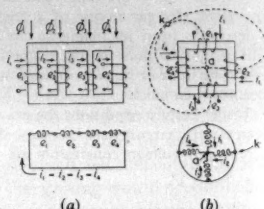


Figure 2. Ideal transformers and the apparent connection of their windings into "equivalent circuits".

(a) mesh-type transformer;
(b) junction-type transformer.

§ 2. EQUIVALENT CIRCUITS OF IDEAL TRANSFORMERS

Figure 2(a) shows an ideal 4-limb transformer having windings with an arbitrary *equal number of turns*, N , wound on a core of infinite permeability. The limbs, which may have different cross-sections, carry fluxes $\Phi_1, \Phi_2, \dots$ which, meeting at a junction, must add up to zero; hence $\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 \dots = 0$. Differentiating and multiplying by N shows that the induced voltages must also add up to zero :

$$e_1 + e_2 + e_3 + e_4 + \dots = 0. \quad \dots\dots(3)$$

Furthermore, the M.M.F.s of the various limbs are in parallel and must be equal, since the transformer is ideal :

$$i_1 = i_2 = i_3 = i_4 = \dots = i. \quad \dots\dots(4)$$

These principles apply to ideal transformers having any number of parallel limbs carrying coils of equal turns.

From equations (3) and (4) the transformer coils may be considered to be connected in an *equivalent circuit* as shown in Figure 2(a); the various coil terminal voltages are in series and a common mesh current i flows. Such an arrangement is not a true "equivalent circuit" in that the impedances of the various coils are

unknown since the original transformer was ideal. This circuit should, at this stage, be regarded merely as a possible pattern into which the various voltages and currents of the transformer windings may be arranged so that the same constraints between them apply as are represented by equations (3) and (4).

A second type of ideal transformer, shown in Figure 2(b), has a series magnetic circuit; the equations for its currents and voltages are

$$i_1 + i_2 + i_3 + i_4 + \dots = 0 \quad \dots\dots(5)$$

$$\text{and} \quad e_1 = e_2 = e_3 = e_4 = \dots = e \quad \dots\dots(6)$$

so that the coils may again be imagined to be connected in an "equivalent circuit", as shown in the lower part of Figure 2(b). Here the terminal voltages are all in parallel and the currents entering the junction point must total zero.*

It may be seen that these circuits can be formed by applying the rules for dual figures, explained in §1, so that meshes in the first circuit are replaced by junction points in the second. In this present ideal case the equivalent electric circuit is the dual figure of the magnetic circuit, as has been illustrated by the superposed dotted circuit in Figure 2(b).

The physically dual quantities are again those which lie on intersecting branches but bear no direct relation to the dual electric impedances of equations (1) and (2). Thus, flux rate of change is dual, here, to voltage, while current is dual to M.M.F. in the intersected limb.†

There again exists a constant of proportion between the quantities in such dual circuits. The duality of these electric and magnetic circuits is clearly reversible. Thus if we had started with the electric circuit we could have obtained the transformer magnetic circuit by drawing the dual geometric figures (shown dotted in Figure 2(b)) and replacing voltage e by flux rate of change $d\Phi/dt$, and current i by M.M.F. M . Thus the duality may be expressed as

$$e \rightleftharpoons d\Phi/dt; \quad i \rightleftharpoons M. \quad \dots\dots(7)$$

One further example is needed to illustrate the complete rules for ideal transformers, viz. a transformer containing both series and shunt limbs. The transformer shown in Figure 3(a) is of such a type and, to make the case more general, two windings are shown on one of the limbs. All coils have N turns. With the fluxes as shown, the relation holds:

$$\Phi_5 = +(\Phi_1 + \Phi_2) = -(\Phi_3 + \Phi_4). \quad \dots\dots(8)$$

The schematic magnetic circuit of M.M.F.s ($M_1, M_2, \dots$) and fluxes has been drawn in Figure 3(b), which also shows the dual figure (dotted lines) drawn according to the rules of interchange of meshes and junction points. On the assumption that this figure gives correctly the "equivalent circuit" of the transformer, it has been redrawn in Figure 4 with the dual currents and voltages marked in. Here the new junction points a, b, ..., k have been identified.

* The directions of the currents in the transformer windings and in the equivalent circuit may be related, if the sense of the coil winding is taken into account. Thus in Figure 2, with the windings as shown, the currents in them are assumed positive in the directions marked; in this case the currents in the equivalent circuits have been made consistent. It is similarly possible to relate the directions of flux rates-of-change and of voltages.

† An arbitrary set of rules could be applied for relating the directions of the currents and of the M.M.F.s in these two superimposed figures. For example, with reference to Figure 3, it could be stated that current direction is positive when it crosses a magnetic branch containing an M.M.F. which is positive on the left-hand side.

That this circuit is correct as regards the two coils on the limb carrying flux Φ_2 follows from the fact that the voltages of the coils are identical, so that they may be regarded as being in parallel with one another. Again, the two limbs carrying fluxes Φ_3 and Φ_4 are magnetically in parallel and their M.M.F.s must be equal, or $M_3 = M_4$; the dual electric branches, a, b and b, k, carry equal currents, being in series.

However, the branch a, k must be shown to be equivalent to that dual limb on the transformer which carries the flux Φ_5 . The voltage across this coil is $Nd\Phi_5/dt$, which, from equation (8) is

$$e_5 = Nd\Phi_5/dt = N(d\Phi_1/dt + d\Phi_2/dt) = -N(d\Phi_3/dt + d\Phi_4/dt) = (e_1 + e_2) = -(e_3 + e_4), \quad \dots\dots (9)$$

and this is seen to be consistent with the mesh arrangement of the equivalent circuit in Figure 4.

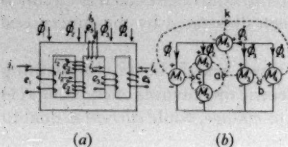


Figure 3. The dual of a multi-limb transformer.
(a) multi-winding ideal transformer;
(b) magnetic circuit (full lines) and the dual figure.

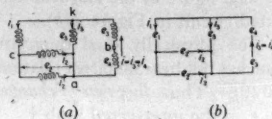


Figure 4. (a) The "equivalent circuit" of the ideal transformer in Figure 3;
(b) the current and voltage pattern.

Other examples may be treated in the same way. No matter how many limbs the transformer may have, or what may be the arrangement of the coils, their connection into an equivalent circuit of the type described may be derived by this routine method of drawing dual figures, provided that: (i) all coils have equal turns, N ; (ii) the transformer magnetic circuit is a planar figure. Similar relations exist between these dual electric/magnetic quantities as between the ordinary electric circuit dual quantities (voltage and current) which have been represented by equation (2). The fluxes (and hence their rates of change) in the various limbs bear certain ratios to one another; the voltages in the (dual) equivalent electric circuit have the same ratios. That is, in the steady state,

$$j\omega\Phi_1 : j\omega\Phi_2 : j\omega\Phi_3 : \dots = e_1 : e_2 : e_3 : \dots \quad \dots\dots (10)$$

A similar relation between the M.M.F.s and currents may be written

$$M_1 : M_2 : M_3 : \dots = i_1 : i_2 : i_3 : \dots \quad \dots\dots (11)$$

The question of magnetic and electric impedance duality analogous to (1) does not arise in these ideal transformers, but will be dealt with in §4.

§3. INCLUSION OF THE EXTERNAL CIRCUIT

When a transformer forms a component part of a circuit it exercises certain constraints on the currents and voltages. These constraints arise by virtue of the magnetic couplings between the transformer windings to which the external

circuit is connected. When the transformer is replaced by an equivalent circuit, this must be arranged so as to exercise the same constraints. In the case of the ideal transformer this equivalent circuit has been derived by applying rules of duality to the transformer magnetic circuit; the external loads and generators must not be included when these rules are applied, but must be imagined disconnected from the transformer windings and then, when the dual figure of the magnetic circuit has been formed, they may be reconnected to corresponding points on this dual circuit so as to support the same currents and voltages as originally.

For example, Figure 5 (a) illustrates an ideal transformer connected to a set of loads and a generator E . This particular transformer has already been used as an example (Figure 3) to illustrate the use of the duality rules, from which it has been shown that the various windings may be considered to form the equivalent circuit connections in Figure 4. This "circuit" is more correctly to be regarded as an arrangement of the various windings, currents and voltages into a pattern which is consistent with the constraints exercised by the transformer. It may alternatively be illustrated by a pattern such as that in Figure 4 (b). The various loads $Z_1, Z_2, \dots$ and the generator E may now be connected in this pattern so as to support the correct voltages and currents. It will be noticed that the resulting circuit (Figure 5 (b)) contains no elements related to the transformer itself since, in this case, this is ideal and possesses no leakage inductance.

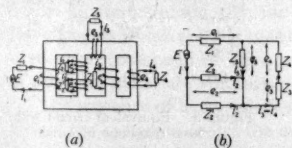


Figure 5. A loaded ideal transformer and its equivalent circuit having identical current and voltage relations.

(a) loaded transformer; (b) equivalent circuit.

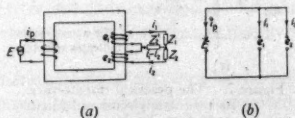


Figure 6. A transformer with interconnected windings and the failure of the "equivalent circuit".

It may sometimes be found that it is not possible to carry out this process as, for example, when there is an external impedance common to two windings. Thus Figure 6 (a) shows a transformer with two secondary windings having equal, induced voltages, e_1 , and common connections between them. The two secondary currents are i_1 and i_2 . The equivalent voltage and current "circuit", or pattern, formed by the dual figure of the magnetic circuit, is given by Figure 6 (b). In this pattern the two secondary voltages naturally appear in parallel and there is no way in which the external circuit Z_1, Z_2 and Z_2' may be connected so as to support the same currents and voltages as in the actual system. In general it is only when each winding is connected to a separate load or generator that connection of such loads in an equivalent circuit is guaranteed. The equivalent circuit pattern merely represents one possible self-consistent arrangement of the transformer winding currents and voltages; an entirely different set of constraints may apply to the external circuit. In any given example it is usually possible to check the existence of an equivalent circuit by forming the dual figure of the transformer magnetic circuit and attempting to reconnect the external electric circuit to this figure, paying due regard to directions of currents and M.M.F.s.

§4. THE PRACTICAL TRANSFORMER—ITS MAGNETIC CIRCUIT

In practice, transformer cores possess finite permeability, and their windings set up leakage fluxes. A practical, loaded, transformer may be regarded either as an electric circuit having a certain arrangement of voltages, currents and impedances or as a magnetic circuit of M.M.F.s, fluxes and reluctances. It is intended now to show that these circuits are duals, as was the case for ideal transformers.

Figure 7(a) illustrates a simple two-winding transformer with primary and secondary leakage fluxes Φ_p' and Φ_s' and a finite core reluctance S , which may possibly include effects of air gaps. The schematic magnetic circuit is given in Figure 7(b). S_p and S_s are the reluctances of the (air) paths of the primary and secondary leakage fluxes.

The current i_p flowing in the N -turn primary coil sets up an M.M.F. Ni_p , which should be regarded as the *driving* M.M.F. M_p . The induced current i_s in the secondary winding gives rise to a *response* or *back*-M.M.F. M_s . The resultant of these M.M.F.s sets up the working core flux Φ .

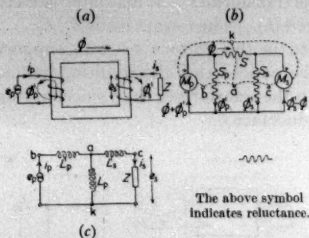


Figure 7. The practical transformer. Its magnetic circuit and (dual) equivalent circuit.

(a) transformer with leakage fluxes; (b) magnetic circuit; (c) equivalent circuit.

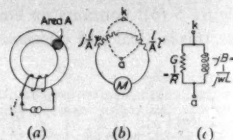


Figure 8. Equivalent circuit with lossy magnetic material.

The dual figure of this magnetic circuit (shown dotted) may now be formed according to the rules, but the question arises: what electric elements are dual to the reluctances? Reluctance causes a loss of M.M.F. proportional to the flux passing through it, $M = \Phi S$; in the (dual) equivalent circuit M.M.F. is replaced by its dual, current, and this must flow through an *electric admittance* to give a drop in voltage, dual to $d\Phi/dt$. This admittance is then the dual of reluctance, and furthermore it must be inductive.

This may be seen more clearly by dividing corresponding sides of equations (10) and (11):

$$\frac{M_1}{j\omega\Phi_1} : \frac{M_2}{j\omega\Phi_2} : \frac{M_3}{j\omega\Phi_3} : \dots = \frac{i_1}{e_1} : \frac{i_2}{e_2} : \frac{i_3}{e_3} : \dots,$$

that is, the ratio between the various magnetic impedances is the same as the ratio between the corresponding electrical admittances. If the electrical elements be *inductances* this last equation may be written

$$\frac{M_1}{j\omega\Phi_1} : \frac{M_2}{j\omega\Phi_2} : \frac{M_3}{j\omega\Phi_3} : \dots = \frac{1}{j\omega L_1} : \frac{1}{j\omega L_2} : \frac{1}{j\omega L_3} : \dots,$$

so that the *duality relation is independent of frequency*:

$$S_1 : S_2 : S_3 : \dots = 1/L_1 : 1/L_2 : 1/L_3 : \dots$$

It is seen that once again there exists a reciprocal relationship between the dual physical elements, S_n and L_n , just as in the case of electrical duality, where the dual impedance elements Z_n and $1/a_n$ were reciprocals (§ 1), since

$$S_n = Ni_n/\Phi_n \text{ and } L_n = N\Phi_n/i_n \text{ or } S_n L_n = N^2. \dots\dots(12)$$

The equivalent circuit for the practical transformer, in the example, has been drawn in Figure 7(c). This equivalent circuit is, of course, well known. The values of the inductance elements are given directly from the values of the dual magnetic reluctances from which they were derived: L_p is dual to S , and so $\propto \Phi/(i_p - i_s)$; L'_p is dual to S_p , and so $\propto \Phi'_p/i_p$; L'_s is dual to S_s , and so $\propto \Phi'_s/i_s$. Note that this equivalent circuit, obtained by the duality rules, is still correct if the secondary be open-circuited or short-circuited. In the first case $i_s = 0$ and the M.M.F. M_s vanishes; that is, it is magnetically *short-circuited*. In the second case $e_s = 0$ and the flux $(\Phi'_s - \Phi)$ vanishes; that is, $\Phi'_s = \Phi$ and the magnetic branch (containing M_s) is open-circuited.

The equivalent electric circuit of any other practical transformer is related to its magnetic circuit in this same dual way, whatever the arrangement of the limbs, provided that the magnetic circuit (including leakage flux paths) forms a planar figure.

§ 5. PRACTICAL TRANSFORMER—INCLUSION OF CORE LOSS

To be correct practically, the magnetic circuit of a transformer must include loss elements which are due to the core hysteresis and eddy currents. The values of such core losses and effective permeabilities are known for many common types of magnetic material (Macfadyen 1947).

The presence of hysteresis loss in a magnetic sample is indicated by the finite area of the hysteresis loop; the average loop is of such a shape as to necessitate a non-linear relationship between $\mathfrak{B}$ and $\mathfrak{H}$, but if the production of harmonics be ignored then, as far as fundamental components are concerned, the hysteresis loop may be regarded as a thin ellipse. This elliptical shape is actually approached in practice if the effects of eddy currents are appreciable. Thus both $\mathfrak{B}$ and $\mathfrak{H}$ may be taken as having sinusoidal waveforms slightly displaced in phase, a point of view which has been adopted by Macfadyen (1947) in the development of the idea of complex permeability.

It is convenient to use this idea here and to regard the magnetic circuit elements, reluctance and "magnetic loss", as complex magnetic impedances, $\tilde{S}$.

The simplest magnetic circuit that may be taken for illustration is a ring having a mean magnetic path length l and a cross-section A (Figure 8(a)). The reluctance of this core, $\tilde{S}$, is related to the permeability, $\tilde{\mu}$, by the expression $\tilde{S} = (l/A)(1/\tilde{\mu})$ amp-turns/weber (henries⁻¹) = $(l/A)(\tau + j\psi)$. These real and imaginary series components of reluctance are illustrated in the magnetic circuit of figure 8(b).

If a coil of N turns be wound on this core, carrying a sine-wave current, i , and having an induced sine-wave voltage, e , the magnetic field-strength and flux-density become

$$\mathfrak{H} = Ni/l \text{ amp-turns/m.}, \dots\dots(13)$$

$$\mathfrak{B} = -je/\omega NA \text{ weber/m}^2, \dots\dots(14)$$

assuming that the $\mathfrak{B}/\mathfrak{H}$ loop is elliptical.

Dividing corresponding sides of (13) and (14) relates the magnetic reluctivity to the electric admittance: $1/\tilde{\mu} = (\tau + j\psi) = jN^2\omega A/l\tilde{Z}$ metres/henry. Thus an equivalent electric circuit may be found for the coil, shown in Figure 8(c), which includes the effects of the complex reluctance $\tilde{S} = (l/A)(\tau + j\psi) = jN^2\omega(G - jB)$ amp-turns/weber (henries⁻¹). Here the electric circuit is given as an admittance $1/\tilde{Z} = (G - jB)$ shown in the figure as a resistance R in parallel with an inductance L . Comparison of the real and imaginary parts of the above equation for $\tilde{S}$ shows that: (i) the *real part* of the reluctance $\tilde{S}$ gives rise to a *susceptance* B , in the equivalent circuit: $l\tau/A \propto B = 1/\omega L$ (as has been shown already for the loss-less core); (ii) the *imaginary part* of the reluctance $\tilde{S}$ gives rise to a *conductance* G , and $(l\psi/A) \propto G (= 1/R)$.

Notice that this equivalent circuit depends on angular frequency ω and so may be applied only to transformers working at a constant frequency.

This electric circuit, Figure 8(c), is the dual of the magnetic circuit, Figure 8(b); the two electric elements in parallel correspond to the two magnetic elements in series. However complicated the magnetic circuit of a transformer may be, such an equivalent electric circuit for each limb may be derived.

§6. THE MULTI-WINDING PRACTICAL TRANSFORMER

It is interesting to apply the method of duality to setting up the equivalent circuits of multi-winding transformers and to show that, in the general case, there can be no physical circuit if the transformer has four or more windings.

Figure 9(a) shows a transformer with one primary and two secondary windings, assumed to be coupled not only by the main working flux Φ but also each to each by leakage fluxes. A possible fourth winding has been shown by dotted lines. In (b) the equivalent magnetic circuit is shown; here the M.M.F.s $M_p, M_1, M_2, \dots$ are those due to the currents in the primary and in the secondary windings. These various M.M.F.s are shown coupled by leakage reluctance paths which are denoted by suffixes: thus S_1 is a reluctance shunting M_1 whereas S_{12} couples M_1 and M_2 , and so on. The addition of the fourth winding to the magnetic circuit is shown by the dotted lines; a new secondary M.M.F. M_3 is coupled to the others by reluctances S_{123}, S_{23} , etc.

Considering the 2-secondary case only, the equivalent electric circuit may be constructed dually in the usual way, by marking in reference points in every magnetic mesh and joining up to form the dual circuit (Figure 9(c)). The various inductances in this circuit are marked by suffixes corresponding to the various appropriate (dual) leakage reluctances, their respective magnitudes being given by equation (12).

In the case of three secondaries, however, such a dual equivalent electric circuit cannot be formed because the magnetic circuit is a non-planar figure. The case considered here includes every possible arrangement of mutual couplings of the windings by leakage fluxes; equivalent circuits of multi-winding transformers have, however, been developed using negative elements. (For example see Blume, Camilli, Boyajian and Montsinger, 1938.) That this figure must be non-planar follows from the topological fact that five or more points in a plane (i.e. the M.M.F. "terminals") cannot be joined each to each by lines (i.e. leakage reluctance paths) without at least one cross-over. Such an essential cross-over is

marked * in Figure 9(b). This fact depends only on the number of M.M.F. "terminals" and not on how they are arranged in the magnetic circuit.

§7. TRANSFORMERS WITH UNEQUAL TURNS ON THEIR WINDINGS

If the principle of duality is to be applied to the construction of equivalent circuits for practical transformers, those cases cannot be excluded in which the turns ratios between the various windings are not unity.

The duality relationship which exists between the magnetic and the electric circuits of a transformer has been established in the preceding sections by starting with the ideal transformers of the "mesh type" and "junction type", illustrated

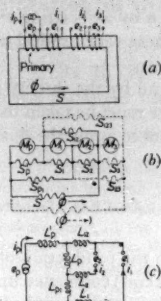


Figure 9. (a) A transformer with three windings; (b) its magnetic circuit; (c) the equivalent electric circuit and (dotted) the effect of adding a fourth winding.

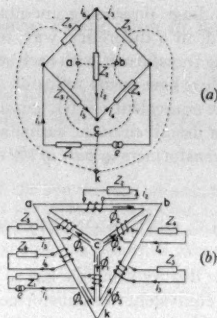


Figure 10. (a) A bridge circuit and (dotted) its dual figure; (b) the dual transformer and its loads.

in Figure 2; the equations (3), (4), (5) and (6), which give the current-voltage or M.M.F.-flux relations, involve the necessary condition that all the coils have an equal number of turns, N . If the coils have an unequal number of turns, these equations are modified. Thus if, in the mesh-type transformer, the limb fluxes, $\Phi_1, \Phi_2, \Phi_3, \dots$ link with coils having, respectively, $N_1, N_2, N_3, \dots$ turns, then equations (4) and (5) modify to $N_1 i_1 = N_2 i_2 = N_3 i_3 = \dots$, that is all limb M.M.F.s, being in parallel, are equal, and similarly $e_1/N_1 + e_2/N_2 + e_3/N_3 + \dots = 0$, since the sum total of the limb fluxes must be zero.

The above equations may be divided by n , the highest common factor of $N_1, N_2, N_3, \dots$, giving

$$\frac{i_1 N_1}{n} = \frac{i_2 N_2}{n} = \frac{i_3 N_3}{n} = \dots \quad \text{and} \quad \frac{e_1}{N_1/n} + \frac{e_2}{N_2/n} + \frac{e_3}{N_3/n} + \dots = 0.$$

These equations represent the voltage and current relations that exist in various "sections" of the individual coils, where one "section" is assumed to have n turns. Then, treating each section as a separate coil, the dual figure may be constructed and a nominally equivalent circuit to the transformer obtained. Such a circuit cannot, however, be the true equivalent circuit, because the n -turn sections into which the coil on a particular limb has been divided are electrically in

series on the limb but are in parallel in this nominally equivalent circuit; the voltages across the transformer windings, which are proportional to the turns $N_1, N_2, N_3, \dots$, do not appear in this equivalent circuit at all.

Again, a junction-type ideal transformer may be treated in a similar way, and in this case, too, no truly equivalent circuit can be derived.

In the case of practical transformers, with cores of finite permeability (possibly complex) and having leakage fluxes, true equivalent circuits consisting entirely of practical electric elements cannot be formed unless all windings have equal numbers of turns. However, by the inclusion of *ideal* transformers in these equivalent circuits the usefulness of the duality relationship may be extended to transformers with non-unity turns ratios. Thus if such a practical transformer has windings possessing unequal numbers of turns $N_1, N_2, N_3, \dots$ these may be reduced, in a theoretical way, to an equal number n by associating an ideal two-winding transformer with each separate winding; these various ideal transformers must then have turns ratios of $N_1/n, N_2/n, \dots$.

The equivalent electric circuit may now be found by the duality rules in the manner described in the earlier sections, though care must be taken to include the ideal transformers *as part of the external loads* and not to apply the duality rules to them.

§ 8. INVERSION OF THE MAGNETIC-ELECTRIC DUALITY PRINCIPLE

The duality principle has so far been applied to the production of an electric circuit equivalent to a transformer (i.e. a magnetic circuit) connected up to external loads and sources of power. As with other dual relationships, such, for example, as the electric circuit duality described in § 1, the procedure may be inverted and, given a planar circuit of purely electric impedances and sources of power, an *equivalent transformer* may be constructed. That is to say, these electrical impedance elements may be assembled on to a transformer in such a way that the constraints between the various currents and voltages are unchanged. That such an inversion of the process is possible has been shown in § 2 and expressed by equation (7).

By way of example, Figure 10 (a) shows a bridge circuit of any linear complex impedances $Z_1, Z_2, Z_3, \dots, Z_6$, carrying branch currents $i_1, i_2, i_3, \dots, i_6$. One source of power is included, for generality, in series with Z_1 . The dual figure may be formed by marking reference points inside every mesh a, b, c, ... with one outside, k, and joining up by lines (shown dotted) intersecting every branch of the circuit. This dual figure gives the required arrangement (Figure 10 (b)) of the transformer limbs and windings which are loaded by the same impedances, $Z_1, Z_2, \dots, Z_6$. In this transformer the various limb fluxes are dual to the circuit branch voltages (more correctly, the flux rates of change if non-steady-state is considered) while M.M.F.s are dual to the branch currents in corresponding (crossing) branches.

Such a transformer is in general ideal, the core having infinite permeability and the number of turns on every winding being arbitrary, but equal. A practical transformer may only be derived *if the original circuit contains inductances* so that the various limbs, dual to the circuit branches, may possess finite reluctances.

Obviously, if the original electric circuit is a non-planar one, possessing cross-over branches, it has no dual figure and, therefore, cannot be assembled on a

transformer in this way. However, part of the circuit may be planar, and those particular branches may be dealt with in the manner described and replaced by an equivalent transformer.

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An Investigation of the Dynamic Elastic Properties of Some High Polymers

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ABSTRACT. An apparatus for the investigation of the transmission of sound along filaments at frequencies between 1,000 and 6,000 cycles per second is described, both for unstrained specimens and whilst they are being elongated at a constant rate of increase of strain. Measurements of the dynamic elasticity and damping factors of filaments of polythene, neoprene and nylon have been obtained, and the correlation of these results with the molecular re-arrangements which take place during stretching is discussed.

§1. INTRODUCTION

THE properties of long chain polymers differ in many ways from materials composed of smaller molecular units and, in particular, the mechanical behaviour is considerably modified when the molecular chains become oriented. Thus the stress-strain curve for such materials is complicated by orientation produced on applying stresses. In general the elastic moduli are found to be much greater for highly oriented materials than for such materials in the isotropic state.

Also, with most of these substances if the stress is applied slowly, irreversible flow takes place, and the strain is a function not only of stress but of time.

The ordinary stress-strain curves of such materials do not, therefore, easily yield information about the molecular processes which take place during deformation.

Some workers have applied alternating stresses of various frequencies to high polymer specimens and measured the resulting strains in efforts to obtain more complete knowledge of the mechanical behaviour of these materials. Recently, measurements of sonic and ultrasonic velocities in fibres of various long chain materials have been made in the U.S.A. by Ballou and Silverman (1944) and Nolle (1947). The work described here extends the scope of this type of investigation by determining the behaviour of filaments under conditions of steadily increasing strain. It was hoped in this way to separate the "elastic" and "plastic" components of strain, and so help to correlate the mechanical properties with the molecular re-arrangements which are known to take place when these substances are deformed.

The method used was to send a sonic wave down a filament of the material, and to measure the velocity of propagation, V . From this the dynamic value of Young's modulus, E , could be determined, using the relation $V = \sqrt{E/\rho}$ where ρ is the density of the material. At the same time, the attenuation of the wave gives a measure of the "internal friction".

In order to measure the variation of these constants with the amount of orientation present in the material, the filament was stretched at a constant rate of increase of strain, and observations made during extension.

It may be shown (e.g. Rayleigh 1896 a) that for the propagation of longitudinal oscillations along a cylindrical specimen, if the wavelength of the oscillations is large compared with the diameter of the cylinder, as in these experiments, then the wave propagation is essentially planar and the linear modulus, E , is applicable.

Since the direction of propagation is along the direction of orientation, the anisotropy will not affect the nature of the wave motion, the relevant modulus being that along the filament.

§ 2. APPARATUS

The apparatus (Figure 1) was designed to measure the velocity of longitudinal oscillations in filaments (about 1 mm. diameter) at frequencies between 1,000 and 6,000 cycles per second; a measure of the absorption of sound along the filaments could also be obtained.

The source of sinusoidal oscillations was a resistance capacitance bridge oscillator as described by Clifford (1945). The advantages of this circuit are great stability and high voltage output. Variation of frequency was obtained by altering the capacities of a Wien bridge. These were ganged air condensers, and adjustment was made through a 6:1 reduction drive so that fine control was possible.

The output from this oscillator was fed into a two-stage R.C. coupled amplifier. The first stage was a Schmitt phase splitter, and the second and output stage consisted of four 6L6 valves wired in a parallel push-pull. These valves were worked as triodes by connecting the screens through 100 ohm stoppers to the anodes and each valve was biased so as to work in Class A. The distortion produced was thus extremely small. A matched transformer coupled the output from this amplifier to the moving coil of the mains-energized speaker. As a check, both the current and voltage wave-form in this coil were examined on a cathode-ray oscillograph, and no distortion from the sine wave input could be detected.

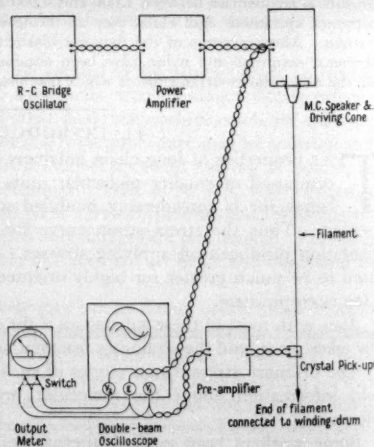


Figure 1.

Figure 2 (a) shows the construction of the Perspex cone which was an integral part of the coil former and which served to transmit the oscillations to the filament. A stiff brass diaphragm carried this system in the centre of the speaker field. By careful centring it was possible to ensure that only longitudinal oscillations were produced.

A crystal gramophone pick-up was mounted on an optical bench, fixed in the direction of the filament so that the position of the pick-up could be varied over a distance of about $1\frac{1}{4}$ m. from the source of oscillation. A difficulty encountered in early experiments was the great change in the cross-section of the filaments when extended to 200 or 300%, so that a fixed contact needle became too loose for large extensions. To overcome this, a Perspex needle with a spring-loaded contact was designed, whereby contact closed on the filament as the cross-section decreased (Figure 2 (b)). The small voltage output from the

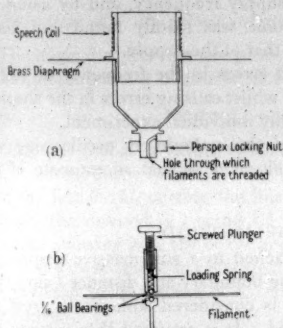


Figure 2. (a) Perspex coil former and driving cone.
(b) Perspex pick-up needle.

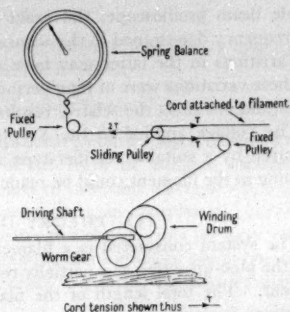


Figure 3.

crystal was amplified by a single stage pentode amplifier located near to the actual pick-up. This was of conventional R.C. type. The output from this was then carried by a screened lead to a Cossor double beam oscilloscope, model 339, and fed through the two stage amplifier incorporated in this instrument on to the Y_1 plates. The screening of the first amplifier was very thorough, as was the decoupling of it from the oscillator and amplifier. Even so, a small amount of 50 c/s. mains ripple was found to be present, and a three element high pass R.C. 'T' filter was placed in the lead from the pre-amplifier to the cathode-ray oscilloscope; this was found to be very effective in eliminating these lower frequencies.

The voltage applied to the speaker coil was carried by screened lead to the other Y plates of the oscilloscope, no amplification being necessary. By adjustment of the time-base and synchronizing control, the trace length could be adjusted so that a single wave corresponded to any set distance on the tube. Phase difference between the two traces could then be measured as the distance between corresponding parts on the two sine waves. Any residual differences of phase, due to amplifiers, etc., were eliminated by the system of measurement, whereby a series of measurements of phase shift against distance along the filament was made.

The free end of the filament was joined to a fine cord which was attached to the drum and tension measuring instrument at the far end of the bench (5 m. from the source). The principle of this instrument is shown in Figure 3. The spring balance was calibrated by loading the cord with known weights. The drum was driven by a $\frac{1}{4}$ h.p. induction motor through a double worm reduction gear which could be varied, the system being effectively synchronous. The gearing used in these experiments was such that the end of the filament was drawn at the rate of 0.194 cm/sec. Whilst the filament was being stretched, photographs of the cathode-ray oscilloscope were taken at regular time intervals (corresponding to equal intervals of strain) with a 16 mm. ciné-camera, and the film measured later. This enabled much more accurate measurements of phase shift to be made than by direct observation.

The frequency of the oscillator was checked against the supply mains. The oscillator was set on to a harmonic of the supply frequency, and by using the double beam oscilloscope, the exact harmonic was readily found and hence the frequency determined to the accuracy of that of the supply.

Variations in the latter may have caused errors in the frequency of 1-2%, but these variations were of long period and, whilst causing errors in the absolute values, did not affect the relative results for any individual experiment.

The voltage applied to the Y_1 plates of the cathode-ray oscilloscope was measured by a suitable rectifier-type A.C. voltmeter so that an estimate of the damping in the filament could be made.

§3. THEORY OF THE METHOD

The system considered is a filament attached to a stiff massive diaphragm with the pick-up acting as a partially reflecting boundary at a distance l along the filament. The total length of the filament is considered sufficiently great for reflections from its other end to be neglected. It is assumed that varying the position of the pick-up will not affect the amplitude of vibration of the diaphragm, and measurements with the apparatus employed showed that this was so.

Let the displacement of the diaphragm ξ_s be given by

$$\xi_s = A \sin \omega t \quad \dots\dots(1)$$

and the displacement of the pick-up by

$$\xi_p = B \sin(\omega t + \theta) \quad \dots\dots(2)$$

where $\omega = 2\pi$ (frequency). We now need to find B/A , the ratio of the amplitudes, and θ , the phase difference, in terms of the position of the pick-up, l , the reflection coefficient at the pick-up, m , and the propagation constants k and α , where $k = \omega/V$ (V = velocity of sound) and α is the damping coefficient.

During the initial transient stages, reflections of the progressive waves will occur, until a state of equilibrium is reached in which a system of stationary waves is set up in the filament.

In the steady state the system can be represented by the sum of a single progressive wave travelling down the filament and a single reflected wave travelling back.

Let the displacement of the outgoing wave ξ_1 at a distance x along the filament be given by $\xi_1 = ae^{-\alpha x} \sin(\omega t - kx)$; then the displacement ξ_2 of the reflected wave is given by $\xi_2 = -mae^{-\alpha(2l-x)} \sin(\omega t - k(2l-x))$ and the resultant displacement ξ is given by

$$\xi = \xi_1 + \xi_2 = ae^{-\alpha x} \sin(\omega t - kx) - ma e^{-\alpha(2l-x)} \sin(\omega t - k(2l-x)).$$

At the pick-up

$$\xi_p = ae^{-\alpha l}(1-m) \sin(\omega t - kl). \quad \dots\dots(3)$$

At the diaphragm

$$\begin{aligned} \xi_s &= a\{\sin \omega t - me^{-2\alpha l} \sin(\omega t - 2kl)\} \\ &= a\sqrt{\{1 - 2me^{-2\alpha l} \cos 2kl + m^2e^{-4\alpha l}\}} \sin(\omega t - kl + \beta) \quad \dots\dots(4) \end{aligned}$$

where

$$\tan \beta = \{(1 + me^{-2\alpha l})/(1 - me^{-2\alpha l})\} \tan kl. \quad \dots\dots(5)$$

Comparing (3) and (4) with (1) and (2) we see that

$$B/A = (1-m)e^{-\alpha l}/\sqrt{\{1 - 2me^{-2\alpha l} \cos 2kl + m^2e^{-4\alpha l}\}} \quad \dots\dots(6)$$

and $\theta = \beta$ given by (5).

(a) *Estimation of V , the velocity of propagation.*

The angle θ represents the phase difference between the speaker diaphragm and the pick-up and is measured as a function of l . Now

$$\tan \theta = \{(1 + me^{-2\alpha l})/(1 - me^{-2\alpha l})\} \tan kl. \quad \dots\dots(7)$$

For large values of αl this can be written approximately $\tan \theta = \tan kl$ whence $\theta = kl$.

The actual curve obtained from (7) is of the form of damped oscillations about the line $\theta = kl$, cutting the line at points of inflexion where $kl = 0, \pi/2, \pi, 3\pi/2$ etc., the interval in l being $\lambda/4$. Figure 4 gives an experimental curve for polythene showing how the curve approximates to a straight line for large values of l . It can be seen that an accurate determination of the gradient can be obtained. This gradient gives a value of k . Hence, since $V = 2\pi f/k$, the velocity may be determined.

(b) *Estimation of α .*

The expression for the amplitude B/A (eqn. (6) above) is more complex. A graph of B/A against l takes the form of damped oscillations (cf. Figure 5). The rate of decay and the number of oscillations present depended on both α and m . For large values of α such as occurred with neoprene, the expression can be simplified to $B/A = e^{-\alpha l}$. This enables a direct value of α to be obtained from a logarithmic plot of amplitude against distance.

For smaller values of α the following method was used. Equation (6) can be written

$$\begin{aligned} \frac{A^2}{B^2} &= \frac{1 + m^2e^{-4\alpha l} - 2me^{-2\alpha l} \cos 2kl}{e^{-2\alpha l}(1-m)^2} \\ &= \frac{e^{2\alpha l}}{(1-m)^2} + \frac{m^2}{(1-m)^2} e^{-2\alpha l} - \frac{2m}{(1-m)^2} \cos 2kl. \quad \dots\dots(8) \end{aligned}$$

For large values of αl the second term vanishes and the expression for A^2/B^2 is of the form of small oscillations about an exponential rise. From (8), neglecting the second term for high values of αl ,

$$\ln(A^2/B^2) = 2\alpha l + C.$$

Thus α is determined by the slope of the graph of $\ln(A^2/B^2)$ against l .

None of these methods could be employed during the drawing of the filaments as the data available from one measurement were insufficient to give a value of α .

§4. EXPERIMENTAL PROCEDURE

In carrying out an experiment the following procedure was adopted. One end of the filament was attached to the cone and the other end to the cord; the motor was then run until the filament was just taut. Measurements of phase and amplitude were then made with the pick-up, at centimetre intervals along the filament. Figures 4 and 5 show the type of results obtained. From these measurements, both V and α for the unstretched filament could be determined.

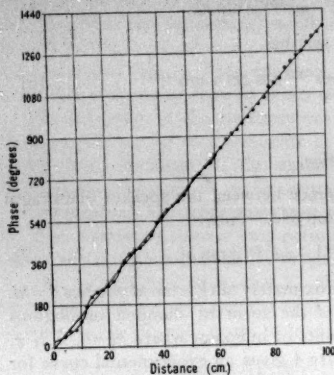


Figure 4. Polythene 3,000 c/s.

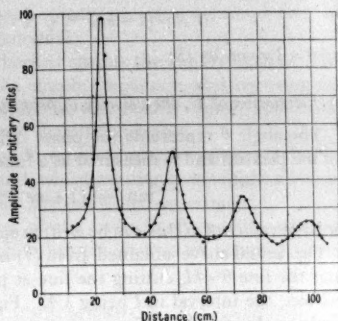


Figure 5. Polythene 1,500 c/s.

In order to measure the variation of the velocity of sound with strain, the pick-up was then fixed at a sufficient distance along the filament for the approximate relation $\theta = kl$ to hold. The motor was started and readings of the spring balance and photographs of the cathode-ray oscillograph trace taken at convenient intervals of time.

In the case of nylon, where the damping was extremely low, the approximate form of the relation between phase and distance along the filament was found to be inaccurate and the accurate form

$$\tan \theta = \left\{ (1 - me^{-2\alpha l}) / (1 + me^{-2\alpha l}) \right\} \tan kl = P \tan kl$$

had to be used.

In general, values of α were not obtained whilst the filament was being stretched. In the case of neoprene, however, a separate set of experiments was made in which the filament was stretched by various amounts, held there, and a separate determination of V and α made as above. This was possible for neoprene as the plastic flow was not so rapid as to invalidate the results. All the experiments were carried out at room temperature; this is stated with the results.

§5. EXPERIMENTAL RESULTS

(i) *Polythene (polymerized ethylene)*. Results were obtained for filaments of polythene of approximately 0.6 mm. diameter. Prior to testing, batches of three lengths were placed in a glass tube five feet long, and kept in a long oven

at a temperature of 90° c. for several days, and then allowed to cool slowly, free from restraint, in a horizontal position.

The filaments were stretched at a rate of 0.0015 per second. Results for the velocity of sound and for the dynamic modulus of the material are given in Table 1 and the dynamic modulus is plotted against strain in Figure 6. From the values of the tension built up in the filament during drawing, values of the true 'static'

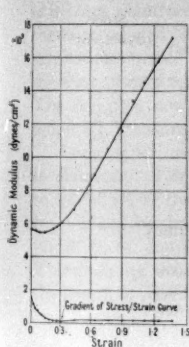


Figure 6. Polythene 3,000 c/s.
Temp. 20°C.

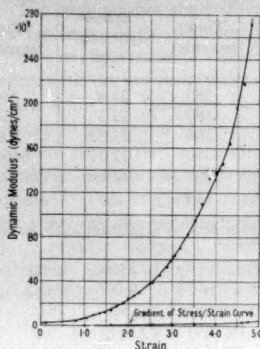


Figure 7. Neoprene 3,000 c/s.
Temp. 20°C.

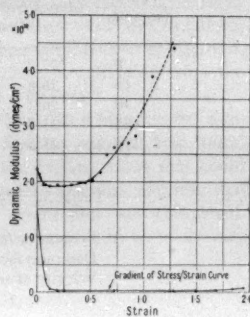


Figure 8. Nylon 3,000 c/s.
Temp. 22°C.

stress were obtained and are also given in Table 1. Values of the gradient of the stress-strain curve, the nominal "modulus", are plotted in Figure 6. A direct comparison between the values for dynamic and static moduli is thus given. In certain experiments the winding machine was stopped when the strain was 1.0, and the relaxation of stress was then measured against time. This is given in Table 2; the change in dynamic modulus during the relaxation of stress was found to be extremely small.

Table 1. Polythene.

(Room temperature 20° c. Frequency 3,000 c/s.)

Strain	Stress (dynes/cm ² × 10 ⁷)	Velocity of sound (m/sec.)	Dynamic modulus (dynes/cm ² × 10 ⁹)	Strain	Stress (dynes/cm ² × 10 ⁷)	Velocity of sound (m/sec.)	Dynamic modulus (dynes/cm ² × 10 ⁹)
0.000	0.459	782	5.65	0.187	10.78	780	5.60
0.014	2.25	782	5.65	0.227	11.32	786	5.70
0.020	2.60	784	5.67	0.267	11.95	797	5.82
0.027	3.58	787	5.70	0.441	15.15	863	6.88
0.033	4.01	787	5.70	0.641	19.71	987	8.98
0.040	4.82	782	5.65	0.774	22.85	1070	10.55
0.053	5.72	780	5.60	0.908	25.8	1122	11.60
0.067	6.53	777	5.56	1.04	28.78	1207	13.41
0.081	7.24	770	5.47	1.11	30.55	1254	14.50
0.094	7.81	770	5.47	1.24	33.50	1286	15.80
0.107	8.51	767	5.44	1.37	36.42	1320	17.20
0.146	9.81	767	5.44				

Most of the experiments were carried out at 3,000 c/s. Some work with undrawn filaments was also done at 1,500 and 6,000 c/s. Values of the damping factor and velocities for these frequencies are given in Table 3.

Table 2. Polythene. Relaxation of Stress

(Strain 1.00. Temperature 20° c.)

Time (seconds)	Stress (dynes/cm ² × 10 ⁷)	Time (seconds)	Stress (dynes/cm ² × 10 ⁷)	Time (seconds)	Stress (dynes/cm ² × 10 ⁷)
0	27.2	280	24.8	2560	22.55
15	26.8	580	23.7	4360	22.22
40	26.2	760	23.58	8000	21.50
65	25.8	1360	22.77	64000	20.20
90	25.5	1960	22.68		

Table 3. Polythene. Variations with Frequency

Frequency (c/s)	1500	3000	6000
Damping factor α (cm ⁻¹)	0.006	0.012	0.033
Velocity of sound (m/sec.)	745	782	811

Table 4. Neoprene

(Room temperature 20° c. Frequency 3,000 c/s.)

Strain	Stress (dynes/cm ² × 10 ⁷)	Velocity of sound (m/sec.)	Dynamic modulus (dynes/cm ² × 10 ⁹)	Strain	Stress (dynes/cm ² × 10 ⁷)	Velocity of sound (m/sec.)	Dynamic modulus (dynes/cm ² × 10 ⁹)
0.10	0.50	133	2.359	3.36	27.61	790	82.7
1.76	7.99	311	12.88	3.52	30.10	845	95.0
1.92	9.15	352	16.5	3.67	34.17	913	110.5
2.08	10.36	412	22.58	3.84	38.10	1000	133.0
2.24	12.20	443	26.35	3.99	41.60	1017	137.5
2.395	13.90	480	30.75	4.16	44.30	1052	146.2
2.56	15.79	545	39.5	4.32	49.30	1110	164.4
2.72	17.85	588	45.9	4.48	53.40	1218	196.8
2.88	20.20	634	53.4	4.64	58.50	1280	218.3
3.04	22.65	692	63.7	4.80	—	1430	271.5
3.19	25.30	726	70.3				

Table 5. Neoprene Damping Coefficient (α)

(Frequency 3,000 c/s.)

Strain	0.06	0.20	0.40	0.80	1.00	1.20	1.40	1.60	1.80	2.00
α (cm ⁻¹)	0.51	0.47	0.44	0.40	0.29	0.19	0.18	0.12	0.07	0.06

(ii) *Neoprene*. The second material investigated was a synthetic rubber Neoprene GN. It was found convenient to strain this material at twice the rate used for the other materials; the rate of straining was thus 0.003 per second. Preliminary experiments showed that this did not affect the results appreciably.

As with polythene, the gradient of the stress-strain curve was calculated. Figure 7 gives a plot of the dynamic modulus and the gradient of the stress-strain curve against strain; numerical results are given in Table 4.

Some results for the damping coefficient were obtained as previously described; these are given in Table 5.

(iii) *Nylon*. Some experiments were also carried out with nylon filaments of 0.7 mm. diameter. For large strains, sharp discontinuities ('necks') appeared; these introduced large variations in the diameters of the filaments and rendered results inaccurate. However, approximate values were obtained and, as before, these are plotted together with the gradient of the stress-strain curve in Figure 8. The damping coefficient α for the undrawn filament was estimated from the amplitude measurements and was found to be about 0.003 cm^{-1} .

Some experiments were also carried out with drawn nylon filament, 0.3 mm. in diameter. The dynamic modulus at 3,000 c/s. for this material was found to be $5.8 \times 10^{10} \text{ dynes/cm}^2$. This is greater than the highest value that could be obtained by drawing the unstrained filaments in the apparatus, showing that under these conditions rupture occurred before orientation was completed. The damping was extremely low and no reliable estimate could be made with the length of filament available.

§ 6. SUMMARY OF RESULTS

The results may be summarized as follows:

1. In the unstretched specimens of all these materials, the dynamic value of Young's modulus obtained from the measurements of the velocity of sound was found to be several times as great as the limiting gradient of the stress-strain diagram.

2. The values of the dynamic moduli for both polythene and nylon, as the filaments were stretched, first showed a slight decrease followed by a rapid rise. In the case of neoprene, however, the dynamic modulus increased steadily.

On the other hand, the gradients of the stress-strain curves for polythene and nylon decrease continually with strain, showing that the effects of plastic flow completely mask the changes in elastic behaviour. For neoprene, the gradient increases but at a much slower rate than the dynamic modulus. The latter had increased more than a hundredfold when the specimen had reached 5.8 times its original length.

3. The results for polythene at 1,500, 3,000 and 6,000 c/s. showed that the damping increases with frequency, whilst there is comparatively little rise in the velocity of sound, and hence in the dynamic modulus.

4. The damping coefficient of unstretched neoprene was found to be very much higher than those obtained for polythene and nylon. Up to a strain of 0.8 the value of the damping coefficient showed little change; for strains greater than this, however, it decreased rapidly and had reached about one-eighth of its original value at a strain of 2.0.

§ 7. CONCLUSIONS

The above results conform, on the whole, to those expected from the molecular models already postulated for these materials from x-ray and other data.

Neoprene, like natural rubber, in the unstretched state, is generally assumed to consist of long molecular chains in a curled-up configuration; when a stress is applied the chains uncurl (Meyer *et al.* 1932, Guth and Mark 1934, Kuhn 1936). The very low value of Young's modulus under these conditions may be attributed to the ease with which rotation may take place around single bonds. When the chains become uncurled, further extension is only possible by changing the bond angles and this will correspond to a very much higher modulus.

The rapid increase in the dynamic modulus with strain may thus be expected to correspond to a decreasing possibility of rotation around single bonds. The large drop in the damping coefficient with extension, previously noted by Cassie, Jones and Naughton (1936) for slow oscillations, might also be expected from the more rigid molecular arrangement in the strained state.

From x-ray data, Bunn (1941, 1942) has deduced that the structures of both polythene and nylon consist of long chains with small crystalline groupings, each of which is made up of portions of several molecular chains. In the unstrained material these have quite random orientations. As the material is stretched the chains become aligned and the crystalline groupings orient along the direction of stretching. When the alignment is completed the material resists further drawing and again behaves in an elastic manner for small extensions.

With the polythene specimens available, it was found impossible to cover the complete stress-strain curve, as the filaments broke before cold drawing was completed. However, measurements were made with unstressed specimens of completely cold drawn nylon filament, which showed that the dynamic elastic modulus was about three times as great as for the undrawn filaments.

The reason for the initial decrease in the value of the modulus, on stretching, in both these materials, is not altogether clear, but may be associated with the breaking up of random crystalline groupings on stretching. Thus, for small strains, the molecular chains may be able to move more freely than in the unstrained material. Further increase in the strain will cause new groupings to be formed with their axes parallel to the direction of stretching.

The frequency variation of the damping coefficient for polythene is in qualitative agreement with that expected from theory (Rayleigh 1896b, Bergmann 1938). The frequency range covered, however, was too small to derive any exact quantitative relations. At higher frequencies the period of the oscillations would become comparable with the relaxation times of the molecular chains, and it is intended to investigate this by extending the frequencies to these higher values.

The large divergence between the static and dynamic moduli in the unstretched filaments may be due to similar effects and to the adiabatic conditions existing in the dynamic measurements.

The thermodynamics of long chain systems has not been fully investigated, and it is hoped that a study of the dynamic properties of these materials under varying conditions of temperature and frequency will add to our knowledge of this subject. Work is now continuing on these lines.

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A Theory of the Angle of Contact

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ABSTRACT. It does not appear to be possible to give a quantitative account of the angle of contact of a continuous liquid in terms of cohesive forces. By using Young's energy relation and making allowance for the effects of adsorbed films on the surface of the solid, expressions are derived for the advancing and receding angles, and a general explanation of the hysteresis of the angle of contact is put forward.

§1. INTRODUCTION

As is well known, there exists no satisfactory theory of the angle of contact between a liquid and a solid. Qualitatively, the existence of an angle of contact has been accounted for in terms of cohesive forces. Thus, Newman and Searle (1933) state that an element of liquid lying in the line of contact experiences two cohesive forces, due respectively to the solid and the liquid, whose resultant must be normal to the tangent plane to the free liquid surface. Unfortunately, as is shown below, this conception cannot be made to yield a quantitative account of the phenomenon.

Young's equation expresses the cosine of the angle of contact θ in terms of the surface energies of the liquid-vapour interface, γ_{LV} , the solid-vapour interface, γ_1 , and the solid-liquid interface, γ_2 . Thus,

$$\cos \theta = (\gamma_1 - \gamma_2) / \gamma_{LV} \quad \dots\dots(1)$$

Recently, Doss and Rao (1938) have considered the effect on the surface energy of the adsorbed film of liquid which condenses from the vapour so as partially to cover the free surface of the solid. Assuming the fractional area σ of the solid which is covered by the adsorbed vapour to be unaffected by the subsequent advance of the bulk liquid over the solid, Doss and Rao deduce expressions for γ_1 and γ_2 and find

$$\cos \theta = 2\sigma - 1 \quad \dots\dots(2)$$

Thus it appears from their theory that a zero angle of contact occurs only when the adsorbed layer completely covers the solid. Their concept of a partial adsorbed film, however, marks a definite advance in terms of which we have been able to give some account of the known dependence of the angle of contact on the state of the surface and the direction of motion of the bulk liquid. It appears that the fractional area of the adsorbed liquid film is changed when the bulk liquid advances to cover the solid.

§ 2. COHESIONAL FORCES AND THE ANGLE OF CONTACT

Following the classical conception of cohesional forces, consider a thin wedge of matter contained between semi-infinite planes inclined to each other at an infinitesimal angle $\delta\phi$. The attraction experienced by an element of mass δm , situated on the edge of the wedge, due to the material composing the wedge, is directed into the wedge in a direction perpendicular to the edge, and may be written as $k\delta m\delta\phi$, where k is a constant depending on the material composing the wedge. It follows that the force of attraction exerted by a wedge of homogeneous isotropic material of finite angle α is directed along the bisector of the angle and is of magnitude $2k\delta m \sin \alpha/2$.

Consider now the equilibrium of an element δm lying at the point P in the line of contact of a liquid and a solid (Figure 1). The element δm experiences three forces F_s , F_L and F_V due to the attraction of the solid, liquid and vapour phases respectively. Thus,

$$F_s = 2k_s\delta m; \quad F_L = 2k_L\delta m \sin \theta/2; \quad F_V = 2k_V\delta m \cos \theta/2,$$

where k_s , k_L , k_V denote the specific attractions of the solid, liquid and vapour respectively and θ is the angle of contact. The condition that the resultant force shall be normal to the free surface of the liquid is then

$$F_s \sin \theta - F_L \cos \theta/2 - F_V \sin \theta/2 = 0,$$

from which it follows that $2k_s = k_L + k_V$.

It appears, therefore, that the requirement that the resultant force acting on an element δm should act normally to the free surface does not in any way determine the angle of contact of the liquid, but leads only to a highly artificial result of no value whatever. We must conclude that no definite angle of contact could exist for continuous, homogeneous substances obeying a classical law of cohesion. This result is in marked contrast with the comparable case of surface tension, of which a coherent account may be given along the lines first laid down by Laplace. No doubt, the equilibrium existing in the line of contact between a solid and a liquid involves in reality the balancing of forces directed towards individual molecular centres. In the absence of detailed knowledge of such forces, however, we must be content with a more limited account of the phenomenon in terms of Young's energy equation.

§ 3. SURFACE ENERGY AND THE ANGLE OF CONTACT

Following Doss and Rao, we may suppose that the free surface of the solid is partly covered by a liquid film, both before the bulk liquid advances to cover the solid and after the bulk liquid has receded. Moreover, if the solid surface is only partially covered by condensed vapour, then under normal conditions the remainder is probably covered by an adsorbed film of air and other impurities, while under vacuum conditions a portion of the surface may be actually bare.

In general, therefore, the solid surface may be supposed to consist of a checker pattern of small patches. As the liquid advances or recedes over the solid surface its motion is easy over some patches and difficult over others, depending on the nature of the actual molecular forces. The line of contact is generally irregular and the angle of contact variable from point to point. Indefinite spreading of the bulk liquid would not take place provided the patches of adsorbed liquid were in the nature of "islands" in the layer of adsorbed air. The angle of contact as measured by macroscopic methods is an average value whose cosine can be expressed by Young's equation, provided allowance is made for the fractional areas of the different patches composing the solid surface. In what follows it is assumed that adsorbed films are of sufficient thickness for the interface on either side of the film to possess the full interfacial surface energy characteristic of the substance in bulk.

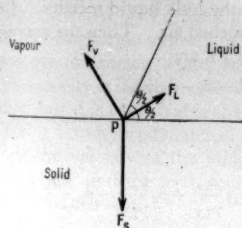
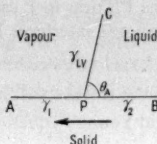
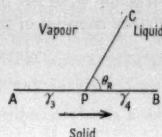


Figure 1.


Figure 2.
Liquid advancing.

Figure 3.
Liquid receding.

Let the surface energies of the interfaces solid-liquid, liquid-vapour, solid-air, liquid-air, air-vapour be denoted by γ_{SL} , γ_{LV} , γ_{SA} , γ_{LA} , γ_{AV} respectively. When the liquid is advancing slowly over the solid (Figure 2) let a fraction σ_1 of the surface PA near to P carry condensed vapour, a fraction ϕ_1 adsorbed air, etc., while a fraction $1 - \sigma_1 - \phi_1$ is bare. Similarly, let a fraction ϕ_2 of the composite solid-liquid interface PB near to P carry adsorbed air, while a fraction $1 - \phi_2$ is a true solid-liquid interface. We cannot assume that $\phi_2 = \phi_1$, since the advance of the line of contact may tend either to compress or partially to remove the layer of adsorbed air. Once the bulk liquid has covered an adsorbed liquid film, no separating interface exists between them. Thus, the average surface energies of the interfaces PA and PB near to P may be written

$$\gamma_1 = \sigma_1(\gamma_{SL} + \gamma_{LV}) + \phi_1(\gamma_{SA} + \gamma_{AV}) + (1 - \sigma_1 - \phi_1)\gamma_{SV},$$

$$\gamma_2 = \phi_2(\gamma_{SA} + \gamma_{LA}) + (1 - \phi_2)\gamma_{SL}.$$

For slow advance Young's equation yields

$$\cos \theta_A = (\sigma_1 + \phi_2 - 1) \frac{\gamma_{SL}}{\gamma_{LV}} + (1 - \sigma_1 - \phi_1) \frac{\gamma_{SV}}{\gamma_{LV}} + (\phi_1 - \phi_2) \frac{\gamma_{SA}}{\gamma_{LV}} + \phi_1 \frac{\gamma_{AV}}{\gamma_{LV}} - \phi_2 \frac{\gamma_{LA}}{\gamma_{LV}} + \sigma_1, \quad \dots (3)$$

where θ_A is the advancing angle of contact.

If it is supposed that the solid surface is perfectly degassed, then $\phi_1 = \phi_2 = 0$, and equation (3) reduces to

$$\cos \theta_A = (1 - \sigma_1) \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) + \sigma_1. \quad \dots (4)$$

If, in addition, the solid is completely covered by a film of liquid condensed from the vapour in advance of the bulk liquid, $\sigma_1 = 1$ and the advancing angle of contact is zero. If, in the other extreme, no appreciable film condenses, $\sigma_1 = 0$ and $\cos \theta_A = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$. This latter expression has been used in the past to define the so-called "equilibrium" angle of contact. According to the foregoing theory, however, the expression defines an upper limit to the contact angle which corresponds to the advance of the liquid over a completely degassed surface and in the absence of any film of condensed vapour on the solid. The actual contact angle for a degassed surface must lie between these theoretical limits and is determined by the value of σ_1 , and hence ultimately by the vapour pressure of the liquid.

Similar expressions may be derived for the receding angle of contact, θ_R . For, let a fraction σ_3 of the surface PA near to P (Figure 3) remain covered by liquid and a fraction ϕ_3 by adsorbed air, etc., when the bulk liquid recedes. Let a fraction ϕ_4 of the interface PB near to P carry adsorbed air. Then the average surface energies of the composite interfaces PA and PB are

$$\begin{aligned}\gamma_3 &= \sigma_3(\gamma_{SL} + \gamma_{LV}) + \phi_3(\gamma_{SA} + \gamma_{AV}) + (1 - \sigma_3 - \phi_3)\gamma_{SV}, \\ \gamma_4 &= \phi_4(\gamma_{SA} + \gamma_{LA}) + (1 - \phi_4)\gamma_{SL}.\end{aligned}$$

For a slowly receding liquid Young's equation gives

$$\cos \theta_R = (\sigma_3 + \phi_4 - 1) \frac{\gamma_{SL}}{\gamma_{LV}} + (1 - \sigma_3 - \phi_3) \frac{\gamma_{SV}}{\gamma_{LV}} + (\phi_3 - \phi_4) \frac{\gamma_{SA}}{\gamma_{LV}} + \phi_3 \frac{\gamma_{AV}}{\gamma_{LV}} - \phi_4 \frac{\gamma_{LA}}{\gamma_{LV}} + \sigma_3 \dots (5)$$

Again, if it is supposed that the solid surface is completely degassed, so that $\phi_3 = \phi_4 = 0$, equation (5) reduces to

$$\cos \theta_R = (1 - \sigma_3) \left(\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \right) + \sigma_3 \dots (6)$$

If a complete film of liquid is left by the receding liquid, whether of macroscopic or microscopic thickness, $\sigma_3 = 1$ and the angle of contact is again zero. On the other hand, if no film whatever remains when the bulk liquid recedes, then $\cos \theta_R = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$. Thus the range of theoretically possible values of the angle of contact against a completely degassed surface is the same whether the liquid is advancing or receding.

§ 4. HYSTERESIS OF THE CONTACT ANGLE

Experiment shows that the advancing angle of contact between water and wax surfaces increases slowly with increase in velocity of the bulk liquid, while the receding angle decreases both with increase in velocity and with increase in the time of immersion (Yarnold and Mason 1949).

Under normal conditions, no part of the solid surface is likely to remain bare. Hence we may write $\sigma_1 + \phi_1 = \sigma_3 + \phi_3 = 1$.

Let us now suppose that the advance of the liquid over the solid is accompanied by a partial removal of the adsorbed air film and a corresponding increase in the fractional area of contact of liquid and solid. Similarly, we may suppose that the recession of the liquid is accompanied by a decrease in the fractional area of contact of liquid and solid and a corresponding increase in the fractional area occupied by adsorbed air. Thus we may write $\phi_1 - \phi_2 = \alpha$ and $\phi_3 - \phi_4 = \beta$, where α and β are themselves functions of the velocity of the bulk liquid. During

immersion, we may suppose that there is a gradual replacement of air by liquid, the air going into solution. Thus $\phi_2 - \phi_1 = \delta$, where δ is a function of time. For the difference in the angles of contact equations (3) and (5) now yield

$$\cos \theta_R - \cos \theta_A = (\alpha - \beta) \left(\frac{\gamma_{SL} - \gamma_{SA} + \gamma_{LV} - \gamma_{AV}}{\gamma_{LV}} \right) + \delta \left(\frac{\gamma_{LV} + \gamma_{LA} - \gamma_{AV}}{\gamma_{LV}} \right). \quad \dots\dots(7)$$

If the time of immersion is very short, the possibility of the solution of air during immersion may be neglected. It follows then that $\delta = 0$ and $\sigma_2 - \sigma_1 = \alpha - \beta$. Thus equation (7) reduces to

$$(\cos \theta_R - \cos \theta_A)_{t \rightarrow 0} = \frac{\alpha - \beta}{\gamma_{LV}} (\gamma_{SL} + \gamma_{LV} - \gamma_{SA} - \gamma_{AV}). \quad \dots\dots(8)$$

Provided γ_{AV} is small, it follows that an increase in the velocity of the bulk liquid is accompanied by a greater hysteresis of the angle of contact. At low velocity the receding angle appears to change more rapidly with change of velocity than does the advancing angle, suggesting that β varies more rapidly than α . At high velocity it is known that the difference of the contact angles attains a constant value, but it is conceivable that no theory of this limiting case is possible without entering into hydrodynamical considerations.

If the velocity of the bulk liquid is constant, the first term of equation (7) is constant, and the hysteresis of the angle of contact increases with increasing time of immersion.

ACKNOWLEDGMENT

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The Angle of Contact Between Water and Wax

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Communicated by L. F. Bates ; MS. received 29th July 1948

ABSTRACT. The effects (a) of the velocity of the liquid surface, and (b) of the time of immersion, on the angle of contact between clean surfaces of water and wax have been investigated by a dynamical method. It is clear that Ablett's measurements are vitiated by the fact that the time of immersion is disregarded. The term "equilibrium angle of contact" appears to be meaningless.

§ 1. INTRODUCTION

A METHOD recently devised by one of us (Yarnold 1946) for the investigation of the hysteresis of the angle of contact has now been used to study the effects of the time of immersion and of the velocity of the liquid on the angle of contact between clean surfaces of water and paraffin wax. The range

of variation of the velocity of the liquid is necessarily quite small, extending only from 0.1 mm. per minute to 1.6 mm. per minute, but the results are of particular interest in that they discriminate clearly between the true velocity effect and the effect of the time of immersion in the case of the receding angle.

§ 2. EXPERIMENTAL

A plane water surface is raised or lowered hydraulically at a definite rate while it is in contact with the surface of a steel sphere coated with paraffin wax and suspended from a Sucksmith ring balance. Continuous observations are made of the force experienced by the sphere and of the position of the water surface. The angle of contact is determined graphically (Figure 1) from the coincidence

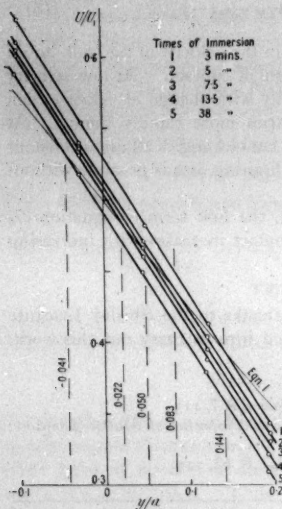


Figure 1.
Receding velocity 1.6 mm/min.

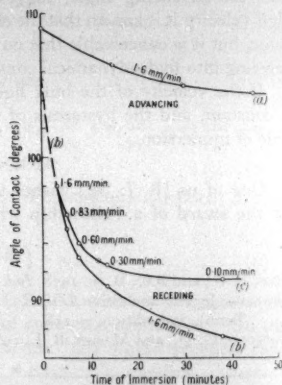


Figure 2.

of the observed upward force with the calculated hydrostatic upthrust on a segment of the sphere, which fixes the position at which the water surface is accurately horizontal right up to the surface of the sphere. Thus, if U is the observed upward force, U_1 the upthrust for complete immersion, y the height of the centre of the sphere above the plane liquid surface and a the radius of the sphere, the necessary criterion is

$$\frac{U}{U_1} = \frac{1}{2} - \frac{3}{4} \left(\frac{y}{a} \right) + \frac{1}{4} \left(\frac{y}{a} \right)^3. \quad \dots (1)$$

The angle of contact θ is then given by the relation $-\cos \theta = y/a$. As has been pointed out previously, the method possesses all the advantages of a dynamical method without the necessity of a knowledge of the surface tension of the liquid. It is therefore more reliable than a purely visual observation of the angle of contact.

The sphere used throughout these experiments was a steel ball-bearing, 0.5 inch in diameter, which was coated by immersion in molten wax to a uniform

thickness of 0.03 mm. The paraffin wax was a high-grade B.D.H. product congealing at 52° c. A fresh wax surface and clean water, freshly swept with waxed barriers, were employed for each individual determination of an angle of contact. The position of the water surface was determined to an accuracy of 0.01 mm. by means of a micrometer needle, so arranged that when contact was established the grid of a triode valve was short-circuited to the cathode and an indication given by a millimeter. The ring balance, employing a double mirror system, was used in conjunction with a telescope and a distant scale. A reading of 4.1 cm. corresponded to a force of 1 gm. wt., while the scale could be read to one-tenth of a millimetre at the velocities employed. In the absence of vibration, individual determinations of the angle of contact of a moving surface were consistent to within half a degree. The velocity quoted is always the velocity relative to the surface of the sphere when the criterion of equation (1) is satisfied.

§ 3. RESULTS

In the velocity range from 0.2 mm. per minute to 1.6 mm. per minute, very little change took place in the advancing angle of contact, the angles observed at these velocities being 108° and 109° respectively. The angles of contact at intermediate velocities were so closely spaced that the assignment of separate values was not justified. The advancing angles quoted for the extreme velocities, however, were based on a very large number of individual runs, with freshly prepared surfaces, and pointed unmistakably to a small but quite definite increase in the advancing angle with increase of velocity.

The effect of the time of immersion on the advancing angle was studied by immersing the freshly prepared sphere in water for various intervals of time immediately prior to the run in which the angle of contact was determined. The curve (a) in Figure 2 shows that for a constant velocity of 1.6 mm. per minute the advancing angle decreased with increasing time of immersion, reaching the value 104.5° after 45 minutes. Observations were not carried beyond this point on account of the risk of contamination of the surfaces.

In dealing with the receding angle of contact, care is necessary to distinguish between the effects of velocity and of time of immersion. At first sight it appears that the receding angle increases with increase of velocity. However, a lower velocity necessarily implies that the waxed surface is immersed in the liquid for a longer period of time before the critical position defined by equation (1) is reached. Hence it is necessary to study the effect of time of immersion alone. Observations were therefore made at the highest velocity (1.6 mm. per minute) after immersing the waxed surface for a suitable period of time prior to the commencement of the run. In the case of the receding angle, this does not of course involve removing the sphere from the water; and the time of immersion is an uninterrupted interval, ending at the instant when the criterion of equation (1) is satisfied.

Figure 1 shows the intersection of the calculated curve representing equation (1) with the experimental curve connecting U/U_1 and y/a . The velocity of the receding water surface is 1.6 mm. per minute in each case, and the effect of increasing time of immersion is very clearly marked. The receding angle of contact at constant velocity is shown as a function of time by curve (b) in Figure 2. Clearly the receding angle decreases very considerably with increasing time of immersion, apparently approaching a limiting value, whose exact observation

would be difficult, however, on account of the risk of contamination of the surfaces during intervals of the order of an hour or more.

The curve (c) in Figure 2 shows the observed receding angles corresponding to different velocities as a function of the time of immersion which is unavoidably associated with the measurement at that velocity. The effect of velocity alone on the receding angle, after particular times of immersion, may be inferred from the difference in ordinate of the two curves (b) and (c). Thus, when the time of immersion is 38 minutes, an increase in velocity from 0.1 mm. per minute to 1.6 mm. per minute is accompanied by a decrease in the receding angle of contact from 91.5° to 87.5° . At lower times of immersion the effect of a change of velocity is less pronounced; and it appears that the greater part of the observed hysteresis is due directly to changes accompanying prolonged immersion. For this reason it appears justifiable to continue curve (b), as indicated by the broken section, up to a receding angle not much less than the corresponding advancing angle of 109° for "zero" time of immersion.

§ 4. DISCUSSION

Comparison with the experiments of Ablett (1923) using the rotating cylinder method reveals a general agreement as regards the change of the advancing and receding angles with increase of velocity. Ablett was able to make observations over a very much wider range of velocity, whereas the present work is confined of necessity to very low velocities. Ablett, however, takes no account of the effect of the time of immersion, though it is clear now that the effect must have been appreciable, at any rate at the lower end of his velocity range. It is apparent also that what Ablett regards as an "equilibrium" angle of contact, and determines during the slow rise of the water past a stationary cylinder, is in reality an advancing angle. In any case, exact numerical agreement with Ablett's work is not to be expected, if only for the reason that his wax surface was prepared by turning in a lathe and ours by dipping in the melted wax. Moreover, Ablett does not appear to have used the sweeping technique in order to obtain a clean water surface.

It is clear from the experiments described in this paper that a definite value can be assigned to the angle of contact of a liquid only if the exact conditions of observation are also specified. In quoting an angle of contact, it is necessary to specify not only the state of the surfaces but also their relative velocity and the time during which they have been in contact. There does not appear to be a single angle of contact corresponding to rest conditions. On the contrary, for relative velocities less than 0.1 mm. per minute in either direction, angles of contact have been observed over the range 91° to 108° . Thus, it appears that the term "equilibrium angle of contact" is practically meaningless. Some theoretical interpretation of the variation of the angle of contact is attempted in a separate paper (Yarnold and Mason 1949).

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The Absorption of Ultrasonic Waves in Liquids and its Relation to Molecular Constitution

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ABSTRACT. Measurements of the absorption of ultrasonic waves in water and ethyl alcohol were made by the pulse method, and are more accurate than those made by other methods. The absorption coefficient α in water was found to vary as the square of the frequency ν over a wide range of temperatures. The measurements in water were made at frequencies between 7.5 and 67.5 Mc/s. and temperatures between 0 and 95° c. The absorption decreased with increasing temperature by a factor of 8 between freezing and boiling points. The observed absorption was about three times that calculated from Stokes' formula and this ratio was nearly independent of temperature. In ethyl alcohol measurements were made at 52.4 Mc/s., and at temperatures between -50° and +60° c. The absorption decreased by a factor of 3 in this range and observed values were about twice those given by Stokes' formula. Values of (α/ν^2) at 25° c. are 22.0×10^{-17} sec²/cm. for water and 50.5×10^{-17} sec²/cm. for ethyl alcohol.

Published values of the absorption coefficients of a wide range of pure liquids and of some mixtures are reviewed, and a classification proposed. The experimental results suggest that the absorption in associated liquids is due to a different mechanism from that in non-associated liquids. In the latter the absorption is probably due to the same phenomenon as in gases: a slow exchange of energy between different degrees of freedom. The relaxation frequencies must be above 200 Mc/s. for most liquids. A simple theory is given to explain the observed variation of the absorption with concentration in mixtures of non-associated liquids. The semi-quantitative agreement of theory with experiment lends support to the relaxation hypothesis.

§1. INTRODUCTION

THE purpose of the present article is twofold. In the first place new measurements of the absorption of ultrasonic waves in water and ethyl alcohol are presented; use of the pulse method enabled the observations to be more accurate and cover a much wider temperature range than previous measurements. In the second place the results obtained by other workers in many different liquids are summarized and discussed. An attempt is then made to classify liquids by the magnitude of the coefficient of absorption and the way in which it varies with frequency and temperature. The significance of the classification is discussed in relation to the molecular species of the liquids and it is shown that a coherent interpretation can be given to what has up to now seemed a diverse collection of data. A simple argument based on the relaxation theory is given to explain the observed variation of absorption with concentration in certain mixtures of liquids.

Both the pressure and amplitude of the sound have been used in the past to define the coefficient of absorption α ; in what follows α is defined by the relation $p = p_0 e^{-\alpha x}$, where p is the amplitude of the excess pressure at a distance x from a

source of plane waves of amplitude p_0 . A quantity having perhaps more physical significance than α is the absorption per wavelength, μ , defined by the relation $\mu = \alpha\lambda$. The quantity μ has the dimensions of a pure number and, provided it is small, is also given by $\mu = \frac{1}{2}\Delta E/E$, where E is the flux of energy per second through unit area normal to the direction of propagation and ΔE the energy per second per unit area absorbed in one wavelength. Measurements of the absorption in gases acquire a greater significance if expressed in terms of μ rather than α , and it is considered that the same may well be true for certain classes of liquid.

Since the development of the acoustic interferometer by Pierce (1925), numerous measurements of the velocity and absorption of sound in gases have been published; these have been summarized by Richards (1939). The results showed that the theoretical treatments of Stokes (1845) and Kirchhoff (1868) were inadequate, and that the measured absorption was considerably greater than that predicted.

This anomaly was treated theoretically by Herzfeld and Rice (1928), Bourgin (1929-1936), Kneser (1931 and 1933) and others, who showed that a large attenuation additional to the Stokes/Kirchhoff value was to be expected, if a time lag occurred in the sharing of energy between the various degrees of freedom in a gas. This "relaxation time" τ was attributed to the sharing of molecular kinetic energy between vibrational motion on the one hand, and translational and rotational motions on the other. An important consequence of the theory is that μ should increase to a maximum value at a frequency ν_m , related to the relaxation time by $\tau = 1/2\pi\nu_m$. The theory also predicts a change in velocity in the same range of frequencies. These two effects have been well substantiated by experiment for polyatomic gases (Richards 1939).

The first measurements of velocity in liquids were those of Freyer, Hubbard and Andrews (1929), and the first reliable work on absorption was that of Biquard (1935). Other data on absorption published in the thirties (cf. Richards 1939) are often not reliable, as indicated by the disagreement between different authors. No conclusive evidence of a change in velocity with frequency was found, but all workers were agreed that the absorption was often much greater than that to be expected from viscosity according to Stokes' formula; in some liquids the observed value of α was 100 times that calculated. (In most liquids the attenuation calculated from thermal conductivity (Kirchhoff 1868) is only a small fraction of that due to viscosity; mercury and liquid helium are exceptions to this).

Many attempts have been made to explain this anomaly for liquids in the same way as for gases, but the absence of the two effects of a relaxation phenomenon mentioned above appeared to be a serious obstacle to the theory.

Kneser (1938) showed however that published observations could be explained by postulating a relaxation phenomenon of a general nature, with a relaxation frequency ν_m so far above the experimental frequencies that the expected dispersion effects would not have been observed.

The problem can now be re-examined in the light of the more accurate experiments which have become available (Willard 1941, Pellam and Galt 1946, Pellam and Squire 1947, Pinkerton 1947). The author's measurements in water and ethyl alcohol described in §2 yield results differing from those obtained by other workers for non-associated organic liquids like carbon disulphide and benzene, in that the absorption is much nearer to the Stokes value and the temperature coefficient is larger and negative.

§ 2. EXPERIMENTAL METHOD AND RESULTS

(i) Method

The experimental arrangement and technique will be described in a separate communication, and it will be sufficient here to indicate the general principle of the method. A short account of the measurements in water has already appeared (Pinkerton 1947).

The pulse method, first described by Pellam and Galt (1946) was developed independently on similar lines by the author from the ultrasonic techniques used for radar during the war. In this method short bursts of ultrasonic oscillations are excited in a quartz crystal. Pulses of ultrasonic waves travel out into the liquid from one face of the crystal, and are returned by a movable reflector. The reflected "echo" is reconverted into electrical oscillations by the same crystal and displayed, after amplification, as a deflection of the trace of a cathode ray oscillograph. Measurement of the amplitude of the echo as a function of range yields a value for α . Due attention is paid to the diffraction effects, which cause a spreading of the beam from the source, and special care is taken to control the temperature of the liquid. The pulse method has the advantage, not possessed by all other methods, that the power transmitted is so small that errors due to local heating and cavitation are negligible.

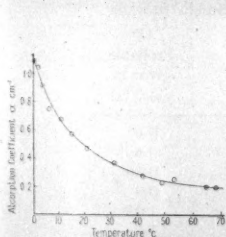


Figure 1. Measured absorption α as a function of temperature in water at 15 Mc/s.

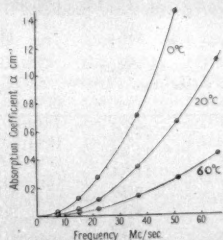


Figure 2. Variation of α for water with frequency ν at various temperatures.

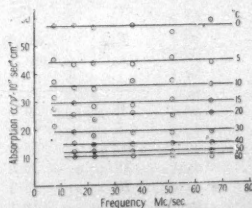


Figure 3. The absorption α/ν^2 for water as a function of frequency and temperature.

Measurements were made over a wide range of temperatures, in water from 0 to +95° c., and in alcohol from -50° to +70° c. The apparatus was also designed so that measurements could be made on several frequencies with the same crystal by the use of harmonics. The frequencies used were approximately 7.5, 22.5, 37.5, 52.5 and 67.5 Mc/s.; a second crystal was used for measurements at 15 Mc/s. Pulses of duration varying from 2 to 20 microseconds were used.

(ii) Results

(a) *Water.* Measurements were made first on 15.0 Mc/s. To obtain a path corresponding to a total absorption of 40 db., a tank 150 cm. long was thought desirable. Unfortunately the losses of heat from so large a tank made it impracticable to observe above 68° c. with the thermostat available. The corrected results at 15 Mc/s. are shown in Figure 1.

In order to find the variation of α with frequency ν measurements were later made at the other five frequencies quoted, at temperatures between 0° c. and

about 60° c. and curves similar to Figure 1 were drawn for each frequency. These curves were used to find the variation of α with ν at the temperature up to 60° c. quoted in Table 1; Figure 2 shows values of α as a function of ν at three different temperatures. The frequency was not always an exact harmonic of 7.5 Mc/s. but was measured separately during each experiment with an absorption wavemeter incorporating a crystal check circuit.

It can be seen that α varies rapidly with ν and a plot of α/ν^2 against ν , shown in Figure 3, indicates that α/ν^2 is approximately constant at constant temperature. The accuracy to which α/ν^2 remains constant can be assessed by using the departures of $[\alpha/\nu^2]_T$ from the mean values to calculate the probable error. The results of these calculations are shown in Table 1 and justify the statement that α/ν^2 is constant to the order of accuracy of our experiments.

For the measurements of α between 60° c. and 95° c. a smaller trough was used to reduce thermal losses, and the shorter path length available restricted measurements to the single frequency of 52.5 Mc/s.

The most striking feature of these results is seen by comparing the observed value of α/ν^2 with that predicted by the theory of Stokes (1845), who showed that $\alpha/\nu^2 = 8\pi^2\eta/3\rho c^3$ where η = coefficient of shear viscosity, ρ = density,

Table 1. Absorption of Sound in Water

Measured values compared with those predicted from Stokes' formula				
(1) T (°c.)	(2) $(\alpha/\nu^2)_{\text{obs}}$ (sec ² /cm. $\times 10^{-17}$)	(3) $(\alpha/\nu^2)_{\text{calc}}$ (sec ² /cm. $\times 10^{-17}$)	(4) $\frac{\alpha_{\text{obs}}}{\alpha_{\text{calc}}}$	(5) Probable error in α_{obs} (%)
0	56.9	17.09	3.33	0.6
5	44.1	13.40	3.29	0.6
10	35.8	11.34	3.15	0.86
15	29.8	9.59	3.11	0.9
20	25.3	8.16	3.10	1.35
30	19.1	6.15	3.10	1.7
40	14.61	4.85	3.01	0.5
50	11.99	3.98	3.01	0.4
60	10.15	3.36	3.00	0.8
70	8.71	2.91	2.99	—
80	7.89	2.58	3.06	—
90	7.24	2.31	3.14	—
100	6.87	2.11	3.26	—

Values of α/ν^2 up to 60° c. are means of measurements at six frequencies in the range 7.5 to 67.5 Mc/s.; values from 60 to 100 are from measurements at 52.5 Mc/s. only. An extrapolation to 100° c. has been made from 95° c.

c = velocity of sound. Column (3) of Table 1 gives the values of α/ν^2 calculated from this formula for various temperatures and column (4) the ratio of observed to calculated absorption. This ratio is strikingly constant over the whole range of temperatures. Values of η and ρ used to find $(\alpha/\nu^2)_{\text{calc}}$ were taken from the International Critical Tables, and the velocity from Randall (1932) whose measurements are probably the best for water.

* This is actually a simplified form of Stokes' result obtained by assuming, on grounds elaborated by him, that any viscosity effects involved in a pure compression could be ignored. The present results may be interpreted as an indication that the second or compressional viscosity is not zero in water or alcohol.

(b) *Ethyl Alcohol*. Since Pellam and Galt (1946) have stated that the absorption in ethyl alcohol is less than is calculated from the Stokes formula, measurements were also made in this liquid. Two samples of alcohol were used; the first contained 6% water and the second not more than 0.5%, and they were investigated at a single frequency of 52.4 Mc/s. The results of the measurements on the dry sample are given in Table 2 in which the values of $(\alpha/\nu^2)_{\text{obs}}$ have been taken from the best smooth curve through the experimental points. The absorption in wet alcohol was the same as in the dry sample at room temperature but rose to a value 30% higher at -30°C .; at $+60^\circ \text{C}$. on the other hand it dropped 5% below that of the dry sample.

The results for the dry sample are compared with Stokes theory in column (7) of Table 2. The velocities of sound for the lower temperatures were obtained by linear extrapolation of the results of Freyer, Hubbard and Andrews (1929), and the values of viscosity interpolated from the results of Tonomura (1933). Above 0°C . the data for η and ρ were taken from the International Critical Tables.

Table 2. Absorption in Ethyl Alcohol

(1) T ($^\circ \text{C}$.)	(2) $(\alpha/\nu^2)_{\text{obs}}$ ($\text{sec}^2/\text{cm} \times 10^{-17}$)	(3) η (poise)	(4) ρ	(5) Velocity ($\text{cm}/\text{sec} \times 10^5$)	(6) $(\alpha/\nu^2)_{\text{calc}}$ ($\text{sec}^2/\text{cm} \times 10^{-17}$)	(7) $\frac{\alpha_{\text{obs}}}{\alpha_{\text{calc}}}$
-50	137.0	0.0630	0.8497	1.418*	68.4	2.00
-40	113.2	0.0475	0.8405	1.382*	56.3	2.01
-30	93.2	0.0367	0.8319	1.346*	47.6	1.94
-20	78.2	0.0287	0.8233	1.311*	40.7	1.92
-10	67.6	0.0226	0.8147	1.275*	35.2	1.92
0	60.4	0.01790	0.8062	1.242	30.5	1.98
10	55.9	0.01451	0.7978	1.204	27.4	2.04
20	52.0	0.01194	0.7893	1.168	24.96	2.08
30	48.7	0.00992	0.7810	1.134	22.90	2.13
40	46.5	0.00831	0.7727	1.101	21.25	2.19
50	44.9	0.00697	0.7633	1.067	19.79	2.27
60	43.7	0.00596	0.7561	1.034*	18.76	2.33
70	42.4	0.00504	0.7470	1.000*	17.8	2.39

* Extrapolated values.

Table 2 shows that the observed absorption is approximately twice the calculated at all temperatures. This result does not agree with that of Pellam and Galt who found absorption less than the calculated value; it agrees, however, with the observations of Willis (1947) within his experimental error. Since the variation of α over the range of temperatures used is 8:1 in water and only about 3:1 for alcohol the constancy of $\alpha_{\text{obs}}/\alpha_{\text{calc}}$ may be considered more remarkable in water.

§3. REVIEW OF PUBLISHED MEASUREMENTS OF ABSORPTION

(i) *Experimental Results for Pure Liquids*

To establish that the absorptions in different liquids are in accord with certain general rules, we now survey the measurements published by other workers, whose values for a variety of liquids are collected in Table 4. Values of α/ν^2 and not α are given and form a fair basis for comparison, since it has been shown for most of the liquids in the table that α/ν^2 is independent of ν (Bär 1937, Grobe 1938, Willard 1941, Rapuano 1947 and others). A decrease in α/ν^2 with increasing ν seems indicated by the results of Rapuano (1947) for carbon

disulphide; at 75 and 105 Mc/s. α/ν^2 was about 1/5 of its value near 10 Mc/s. (Biquard 1935, Willard 1941). α/ν^2 is far from constant for acetic acid, methyl and ethyl acetate and solutions of metallic acetates (Bazulin 1936, 1939, Claeys, Errera and Sack 1937, Pinkerton 1948); a full discussion of these latter cases is not relevant here and will therefore be reserved for a future communication.

With the above exceptions it may be taken as established that α is accurately proportional to ν^2 in most liquids up to 100 or 200 Mc/s. At higher frequencies evidence is lacking except for mercury for which α/ν^2 is constant up to 1,000 Mc/s. (Ringo, Fitzgerald and Hurdle 1947).

The values of Table 4 are taken from Willard (1941) and Pellam and Galt (1946), who measured in all about 50 organic liquids; their results agree within the experimental accuracy claimed, and are confirmed for the commoner liquids by Biquard and others. Results are also available for the two monatomic liquids, helium (Pellam and Squire 1947) and mercury (Bär 1937, Rieckmann 1939, and Ringo, Fitzgerald and Hurdle 1947), in which the absorption was found to agree with the Stokes/Kirchhoff value (helium shows an anomaly near and below the λ -point). Four highly viscous liquids were investigated by Hunter (1941).

The dependence of α on temperature is highly significant for any classification of liquids according to their absorption. This dependence was investigated for many liquids by Pellam and Galt (1946) and also by other workers for a number of individual liquids, viz.: water and alcohol by the author (*supra*), water (Fox and Rock 1946), benzene (Quinn 1946, Bazulin 1937), carbon tetrachloride (Bazulin 1937), four very viscous liquids (Hunter 1941) and liquid helium (Pellam and Squire 1947).

(ii) Classification of Liquids by their Absorption

A previous attempt has been made by Kittel (1946) to classify liquids according to their absorption of ultrasonic waves. A more extensive classification is here proposed based on two criteria: (a) the ratio of observed absorption to the Stokes value, denoted $\alpha_{\text{obs}}/\alpha_{\text{calc}}$; (b) the temperature coefficient of absorption. It is found that, with the exceptions mentioned in § 3 (i), all pure liquids may be assigned to one of the four classes of Table 3.

Table 3

(1) Class	(2) Range of ($\alpha_{\text{obs}}/\alpha_{\text{calc}}$)	(3) Temperature coefficient of α	(4) Type of liquid	(5) Examples
Anomalous A I	1,500 to 3	Positive. ($\alpha_{\text{obs}}/\alpha_{\text{calc}}$) varies with T .	Non-associated polyatomic.	Carbon disulphide; benzene; most non-associated or- ganic liquids.
Anomalous A II	3 to 1.5	Strongly negative. ($\alpha_{\text{obs}}/\alpha_{\text{calc}}$) nearly independent of T .	Associated polyatomic.	Water; alcohols.
Normal N I	1	Positive for helium.	Monatomic.	Helium; mercury.
Normal N II	1	Negative.	Associated polyatomic.	Glycerine; highly viscous liquids.

Table 4 shows a number of liquids listed according to the classification of Table 3; in each class the liquids are quoted in descending order of α/ν^2 .

Table 4

(1) Class	(2) Liquid	(3) (a_{obs}/ν^2) (sec ² /cm. $\times 10^{-13}$)	(4) η (° c.)	(5) $\mu \times 10^3$ at 10 Mc/s.	(6) $(a_{\text{obs}}/a_{\text{calc}})$	(7) Temperature coefficient of a_{obs}	(8) Observer
A I	Carbon disulphide	7,400	23-27	85.0	1,540	—	W.
	Benzene	800	21-8	10.5	100	Positive	P.G. (G.)
	Carbon tetrachloride	533	23-5	4.9	27	Small positive	P.G. (B.)
	Acetylene dichloride	400	23-27	4.1	52	—	W.
	Chloroform	380	23-27	3.8	38	—	W.
	Methyl iodide	316	20	2.6	33	Positive	P.G.
	Chlorobenzene	123	7.5	1.6	12.3	—	P.G.
	<i>n</i> -butyl chloride	108	2.0	1.3	10.8	—	P.G.
	Toluene	90	23-27	1.2	11.5	—	W.
	Nitromethane	90	23-27	1.2	10.4	—	W.
	<i>n</i> -heptane	80	22.4	0.9	8.0	—	P.G.
	Nitrobenzene	79	23.8	1.15	5.6	Positive	P.G.
	<i>m</i> -xylene	78	23-27	1.0	9.6	—	W.
	<i>n</i> -hexane	77	21.2	0.8	7.7	—	P.G.
A II	Acetone	64	23-27	0.8	10.3	—	W.
	Propyl iodide	54	2.0	0.5	3.8	—	P.G.
	<i>n</i> -amyl alcohol	106	28.6	1.3	1.83	Negative	P.G.
	<i>n</i> -butyl alcohol	106.5	2.0	1.4	1.04	Not observed	P.G.
	<i>n</i> -propyl alcohol	70	27.5	0.84	1.95	Negative	P.G.
	Ethyl alcohol	52.0	20.0	0.61	2.08	Negative	Author
	Methyl alcohol	37	19.3	0.41	2.64	Negative	P.G.
	Water	25.3	20.0	0.375	3.10	Negative	Author
	Helium	230	4° K.	0.44	1.1	Positive	P.S.
	Mercury	5.5	27.0	0.08	1.08	Not observed	R.F.H.
N II	Castor oil	34,000	2.7	530	1.1	Negative	H.
	Glycerine	5,200	27	77	1.04	Negative	H.
	Olive oil	4,400	14	85	1.1	Negative	H.
	Cyclohexanol	800	34	15	1.06	Negative	H.
		1,900	9	28	1.05	Negative	H.
		1,350	21.7	19	1.35	—	W.

Key to authors:—P.G. = Pellam and Galt; W = Willard; P.S. = Pellam and Squire; H = Hunter; R.F.H. = Ringo, Fitzgerald and Hurdle; G = Grobe; B = Bazulin. For references see text.

The two anomalous classes of liquids accord well with the more usual distinction between associated and non-associated liquids. Moreover the liquids in class A I with the greatest absorption are those having zero dipole moment and small roughly symmetrical molecules. The introduction of chlorine into the benzene ring to form chlorobenzene destroys the symmetry and lowers the absorption whilst increasing the dipole moment. This tendency is more marked in nitrobenzene whose absorption is still less. In class A II the nearly regular progression of values of α_{obs} from water to amyl alcohol is most striking, although butyl alcohol does not seem to take its proper place in the series, probably because the absorption quoted for this alcohol relates to 2° C. and not to some temperature near 25° C. Even more noteworthy is the fall in the ratio $\alpha_{\text{obs}}/\alpha_{\text{calc}}$ as one ascends the homologous series, water taking the place of an "alcohol" with no carbon atom. It has been mentioned that in water and ethyl alcohol $\alpha_{\text{obs}}/\alpha_{\text{calc}}$ is nearly independent of temperature; sufficient data are not available to test this rule for the other alcohols.

(iii) *Experimental Behaviour of Mixtures*

The absorption of ultrasonic waves in mixtures of two liquids in varying proportions has been investigated in the following cases: mixtures of benzene with toluene (Bazulin 1936, Grobe 1938), carbon disulphide with benzene and with carbon tetrachloride (Claeys, Errera and Sack 1937), and benzene with acetone (Willard 1941). All these liquids are of class A I and are non-associated; acetone and toluene have dipole moments. In each case one of the pure liquids had an absorption about ten times larger than the other.

In all the above cases there was a very rapid decrease in α as the proportion of the less absorbing liquid was increased (cf. Figure 5); further increases in the proportion of the latter had progressively less effect. There was no suggestion of a linear variation with concentration.

Contrasting results were obtained by Bazulin and Merson (1939), Willard (1941) and Willis (1947), who measured the absorption in mixtures of acetone and water, and by Mikhailov (1940) Mikhailov and Gurevich (1946), and Willis (1947) who studied mixtures of water and ethyl alcohol. Mikhailov and Gurevich also studied mixtures of methyl alcohol and water. All these observers found a maximum in the absorption at some intermediate concentration, the maximum absorption being about twice that of the more absorbing liquid when pure.

§ 4. THEORETICAL DISCUSSION

(i) *Possibility of Scattering*

It has occasionally been suggested (e.g. Lucas and Biquard 1937) that the anomalous part of the absorption is due to some scattering process. It is a simple matter to test for scattering using the pulse technique, and special tests were made in water and alcohol free from dust and air bubbles. These tests failed to reveal any scattered sound, although if scattering were to account for any appreciable part of the absorption it should readily have been perceptible under the conditions of the experiment. We conclude that the anomalous values of the absorption coefficient are not due to scattering.

(ii) *The Relaxation Hypothesis*

The relaxation phenomena found in gases and caused in that case by the slow equipartition of energy between different degrees of freedom, will also occur

in any other case where the volume changes of the medium do not follow instantaneously the changes of pressure in the sound wave. Kneser (1938) showed that if a single relaxation process gives rise to absorption in a medium, then the expected variation of α with ν would be of the form

$$\alpha/\nu^2 = A/[1 + (\nu/\nu_m)^2] \quad \dots\dots(1)$$

where A is very nearly constant, and $\nu_m = 1/2\pi\tau$, is the postulated relaxation frequency. From (1) α/ν^2 would be expected to be constant so long as $\nu \ll \nu_m$, and from the experimental values of α/ν^2 Kneser made estimates of the lowest possible relaxation frequency in various liquids. With the data now available his estimates of ν_m would have to be increased in many cases since we know α/ν^2 to be constant up to 100 or 200 Mc/s. in several liquids (Rapuano 1947).

However we may set an approximate upper limit to ν_m as follows; we consider the absorption per wavelength, μ , which from (1) is given by

$$\mu = \alpha\lambda = (\alpha/\nu^2)\nu^2\lambda = Ac\nu/[1 + (\nu/\nu_m)^2] = B(\nu/\nu_m)/[1 + (\nu/\nu_m)^2] \quad \dots\dots(2)$$

where B is a new constant $= Ac\nu_m$, and c is the velocity. Equation (2) shows that, for $\nu \ll \nu_m$, μ increases linearly with ν as on the Stokes theory. When $\nu = \nu_m$ however μ attains a maximum value, $\mu_m = Ac\nu_m/2$. Since A and c are known from experiment, an estimate of μ_m gives a value for ν_m . It is possible to make a reasonable guess at μ_m for a liquid if the absorption is due to slowness of exchanges of energy between degrees of freedom, from the value obtained for μ_m in gases. If this mechanism be accepted μ_m is completely determined by the specific heats C_p and C_v and the fraction of C_v corresponding to internal degrees of freedom (Richards 1939). Since these specific heats probably do not change by large factors on passing from gas to liquid (Herzfeld 1941), we put $(\mu_m)_{\text{gas}} \approx (\mu_m)_{\text{liquid}}$. Values of $(2\mu_m)$ quoted by Fricke (1941) vary between 0.2 and 0.3 for several gases, and in other cases can be calculated from specific heats of the individual degrees of freedom obtained from spectroscopic data.* To find ν_m we take $2\mu_m \approx 0.25$, and therefore from (2), $Ac\nu_m \approx 0.25$ or

$$\nu_m \approx 1/4cA. \quad \dots\dots(3)$$

Here A is the constant value of α/ν^2 found in experiments at low frequencies; tentative values of ν_m calculated from (3) are given in Table 5.

Table 5. Approximate Values of ν_m for $2\mu_m \approx 0.25$

Liquid	ν_m (Mc/s.)	Liquid	ν_m (Mc/s.)
Carbon disulphide	30	Nitrobenzene	2,200
Benzene	240	Ethyl alcohol	4,000
Carbon tetrachloride	500	Methyl alcohol	6,000
Chlorobenzene	1,500	Water	7,000
Toluene	2,000		

The value $\nu_m = 240$ Mc/s. shown for benzene is sufficiently small to deserve comment; measurements were made up to 165 Mc/s. by Rapuano (1947), and in the diagram in which his values are given there seems to be a small but systematic decrease in α/ν^2 up to 165 Mc/s., which does not conflict with our estimate for ν_m .

It is more surprising that the relaxation frequency of 30 Mc/s. predicted for carbon disulphide has not been found experimentally; the drop in α/ν^2

* Unpublished calculations for liquids by Mr. E. Bauer from spectroscopic data have also shown that this is a reasonable estimate for μ_m .

between 10 and 75 Mc/s. mentioned in §3 (i) is partial confirmation, and a more detailed investigation is planned by the author.

The experimental results have therefore been shown to be consistent with the occurrence of a relaxation process at a frequency outside the present range of measurement. The following facts indicate that the relaxation mechanisms are different for the liquids in classes A I and A II.

(i) The temperature coefficient of absorption is positive for class A I and negative for A II. In class A II $\alpha_{\text{obs}}/\alpha_{\text{calc}}$ is nearly independent of T .

(ii) The absorption varies very differently in mixtures of liquids in the two classes.

(iii) Calculations by Herzfeld (1941) showed that the specific heat of the internal vibrations in water is too small to account for the anomaly and that the absorption from this cause should be zero at 4° C. when $C_p = C_v$, which is not true (Fox and Rock 1946).

It is suggested that relaxation of the internal degrees of freedom postulated for gases will account for the anomalous absorption in liquids of class A I. The behaviour of liquids in class A II is probably determined by changes in local molecular order (Hall 1947, 1948). In certain other liquids like acetic acid the absorption may be due to the perturbation of a chemical equilibrium (Pinkerton 1948).

A complete theory of the absorption of sound in liquids in class A I is required to predict ν_m as well as μ_m , but there seems little prospect at present of being able to predict ν_m from independent data. However the theory outlined above implies that the wide variations in α/ν^2 between liquids must be largely due to variation of ν_m , since we have assumed μ_m to be roughly the same in all liquids. From equation (2) it is easily seen that

$$\lim_{\nu \rightarrow 0} (\alpha/\nu^2) = 2\mu_m/c\nu_m. \quad \dots\dots(4)$$

This relation shows that highly absorbing liquids must have small values of ν_m , which implies that they do not readily share their vibrational energy. But this is what we should expect for liquids having small spherically symmetrical molecules with no dipole moment; such liquids should therefore be strongly absorbing. Reference to class A I of Table 4 shows this to be the case. The symmetrical non-polar molecules of carbon disulphide, benzene and carbon tetrachloride show the greatest absorption, while nitrobenzene and propyl iodide show small absorption.

The same general rule was followed in many other liquids omitted from Table 4 for reasons of space.

The frequency of molecular collisions in a liquid is about 10^{12} per second at room temperature (Glasstone, Laidler and Eyring 1941), so that taking the relaxation frequencies to be of the order of those in Table 5, it follows that from 500 to 30,000 collisions are required before the internal and external energies come to equilibrium after an abrupt change in the external conditions. It is noteworthy that in those gases, for which the lifetimes of the excited states are longest, ν_m and therefore the absorption are most sensitive to traces of impurities (Fricke and Knudsen 1941), although μ_m is not greatly affected. It has frequently been suggested that this is due to the impurity acting as a "catalyst" in transfers of internal energy. Such a process may very well also occur in mixtures of two liquids, and is the basis for the argument used below.

(iii) Explanation of the Behaviour of Mixtures

By making certain simple assumptions the relaxation mechanism proposed can be used to calculate approximately the variation of absorption in mixtures of two liquids of class AI. We introduce a relaxation time $\tau = 1/2\pi\nu_m$ where ν_m is the relaxation frequency of equations (1)–(4). In a mixture of liquids A and B, in which the equilibrium between the energies associated with internal and external degrees of freedom is set up by collisions, it is possible to define four relaxation times as follows: τ_{AA} and τ_{BB} are the relaxation times for collisions between similar molecules of types A and B respectively, τ_{AB} is that for collisions of excited type A with de-excited B, and τ_{BA} that for collisions of excited B with de-excited A. Since the absorption in A is much greater than in B we now assume $\tau_{AA} > \tau_{BB}$ and write $\tau_{AB} = \tau_{BA} = \tau_{BB}$. The reason for this is that if molecules of type B possess a stronger mutual interaction, the interaction between A and B molecules may well be of the same order as between two molecules of B, and may be expected to be much greater than the mutual interactions between molecules of type A. Denote the fraction of molecules of type B in the mixture by x , and neglect differences in the molecular diameters, which is justifiable to a first approximation for the liquids on which data are available. Then in unit time a fraction $(1-x)$ of A will collide with molecules of the same kind and have relaxation time τ_{AA} , and a fraction x of A will have relaxation time τ_{BB} , because of collisions of A with B. In a short time Δt the number of molecules A relaxing will be proportional to:

$$\frac{\Delta t}{\tau_{AA}}(1-x) + \frac{\Delta t}{\tau_{BB}}x = \frac{\Delta t}{\tau_{A_{\text{eff}}}}, \text{ say,} \quad \dots\dots(6)$$

where $\tau_{A_{\text{eff}}}$ is the effective relaxation time for molecules type A. Now from the assumption that μ_m is the same in both pure liquids, it follows from equation (4) that, at low frequencies

$$\alpha_A/\alpha_B = (c_B\nu_{mB})/(c_A\nu_{mA}) = (c_B\tau_{AA})/(c_A\tau_{BB}).$$

It will be convenient to assume that $c_A = c_B$, which is true for the case of benzene and toluene. We can then put

$$\alpha_A/\alpha_B = \tau_{AA}/\tau_{BB} = 1/y, \text{ say.} \quad \dots\dots(7)$$

In the mixture the absorption will be additive for the two molecular species and will be given from equation (4) by:

$$\frac{\alpha(x)}{\nu^2} = \frac{4\pi\mu_m}{c} [\tau_{A_{\text{eff}}}(1-x) + \tau_{BB}x]. \quad \dots\dots(8)$$

Substituting for $\tau_{A_{\text{eff}}}$ from (6), and using the conditions that

$$\alpha(x) = \alpha_A, \text{ when } x=0; \quad \alpha(x) = \alpha_B, \text{ when } x=1,$$

we arrive at the result that:

$$\alpha(x) = y \left[\frac{(1-x)}{(1-x)y + x} + x \right]. \quad \alpha_A = P(x, y) \cdot \alpha_A, \text{ say.} \quad \dots\dots(9)$$

This expression gives the proportional variation in absorption in the mixture, in terms of the ratio $1/y$ of the absorptions in the pure liquids, and the molecular proportion x . Both quantities are known from experiment, and no arbitrary parameter need be introduced.

In Figure 4 the relation between P and x is shown for the two arbitrary values of y , 0.3 and 0.1. A detailed comparison with experiment is made in Figure 5 in which the points indicate values found by Grobe (1938) for mixtures of benzene with toluene. The full curve corresponds to $y=0.1$, which is the ratio of the absorptions in the pure liquids.

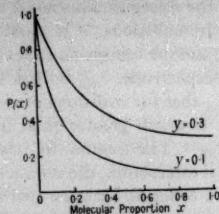


Figure 4. Graph of the function $P(x, y) = y \left[\frac{1-x}{(1-x)y+x} + x \right]$ for $0 < x < 1$, and $y=0.1$ and 0.3.

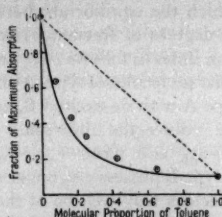


Figure 5. Observed and theoretical absorption in mixtures of benzene and toluene. The curve is theoretical and the points due to Grobe (1938).

The agreement between observed and calculated values is satisfactory in view of the drastic simplifying assumptions made. Equally good agreement is found for the other pairs of unassociated liquids which have been investigated.

This explanation does not fit the case of mixtures of associated liquids at all; the process which is responsible for their behaviour is not clear at present.

ACKNOWLEDGMENTS

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LETTERS TO THE EDITOR

A Note on Magnetic Viscosity in Alnico

Magnetic viscosity occurring in specimens of a high-coercivity alloy, alnico, has already been briefly reported (Street and Woolley 1948). It would appear from further investigations carried out in this laboratory that the experimental results may be satisfactorily accounted for by assuming that, after a sudden change in an external magnetic field applied to the specimen, the movement of the domain magnetization vectors is restricted by energy barriers. Thus the domains may be characterized by a distribution of activation energies, and by using an analysis similar to that of C. L. Smith (1948) for transient creep in metals we find that the total change in the intensity of magnetization, ΔI , at a time t sec. after the change in field has been completed is given by the equation

$$\Delta I = (\text{constant}) T \log (Ct),$$

where T is the absolute temperature of the specimen and C is a constant.

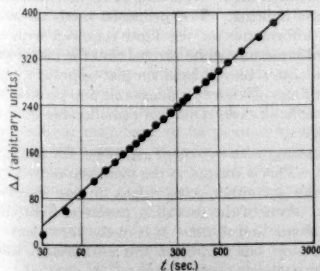


Figure 1. Results for alnico for $H \approx$ coercive field.

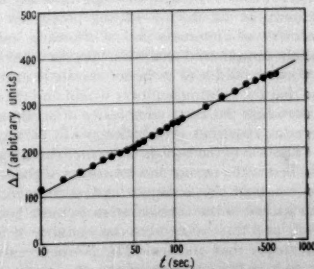


Figure 2. Ewing's results (1889) for soft iron.

It would be expected from this equation that ΔI would be a linear function of $\log t$, and the $(\Delta I, \log t)$ curve obtained with an alnico specimen at its coercive force point (Figure 1) indicates that the experimental results are in satisfactory agreement with this hypothesis over a large range of t . The results of Ewing (1889) for soft iron specimens are represented in the form of a $(\Delta I, \log t)$ curve (Figure 2), and here also a linear variation exists.

Again, the equation predicts that the slope of the (ΔI , $\log t$) curve should be directly proportional to the absolute temperature T of the specimen. Preliminary experiments with an alnico rod seem to support this conclusion.

It is hoped to publish a more detailed account of this work at a later date.

The University, Nottingham.
25th November 1948.

R. STREET.
J. C. WOOLLEY.

EWING, J. A., 1889, *Proc. Roy. Soc. A*, **46**, 269.

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REVIEWS OF BOOKS

Shadow and Diffusion in Illuminating Engineering, by K. NORDEN. Pp. x+165.
(London: Pitman, 1948.) 25s.

The quality of lighting denoted by hardness or softness is a very familiar one. On it depend the sharpness or vagueness of shadows, and the contrasts and prominence of shading which help to reveal the shapes of objects seen. The very great importance of the correct disposition of shadows, and of correct contrasts, is seen in the work of a skilled photographer, or in considering the conditions necessary for the best visibility in various industrial tasks. The recent work of H. C. Weston is notable as having established the relation between contrast and similar factors on the one hand and ease and speed of performance of visual tasks on the other. It has done much to increase the interest of the lighting engineer in the whole subject of the directional properties of lighting systems in relation to the appearance of the objects illuminated. It is not a simple matter, however, to translate the degree of contrast and other factors governing the visibility of an object or task into corresponding factors in the design of a lighting installation as a whole, suitable for inclusion in the engineer's specification. Moreover, the lighting designer has in any case many other factors to think about, such as the level, diversity and colour of the illumination, and glare. He may well claim, therefore, that to try to measure or specify in detail the vectorial distribution of light on the working plane, in any terms but those of a general commonsense empiricism, would be really too much of a good thing.

Much of Dr. Norden's book is an open challenge to this attitude. Dr. Norden proposes a more formal approach, through the study and measurement, according to certain standard methods, of the shadow-casting properties of the lighting. The proposed methods have the merit of directness and of affording useful information of the kind required without unduly complicated analysis. On the other hand it remains to be proved that the use of the methods would lead to better results than those now achieved by a simpler approach, and also that the lighting engineer would find the methods sufficiently manageable and profitable, to outweigh the extra complexity of an already difficult task. One has considerable doubt, therefore, whether the challenge will be accepted.

The rest of the book is concerned, broadly speaking, with two other aspects of the subject. 'The first is the nature and formation of shadows. This is treated in the main geometrically, and many of the examples and calculations given are either self-evident or not original. The second is the consideration in more general terms of the revealing power of light and shade, and their relation to the visibility of fine detail, and so on. It is in the treatment of this aspect that one feels Dr. Norden really arouses one's interest and enthusiasm, and succeeds in his advocacy of the importance of his subject.

Dr. Norden has been known to lighting engineers for many years as a courageous and dogged protagonist of the study of shadows. The fundamental rightness of his course could not now be denied; but on reading this latest publication of his one cannot help wishing that it had been devoted only and entirely to a study of the subject for its own sake, and not with a view to providing new tools for the installations designer. In treating this broader aspect of his subject Dr. Norden combines the analytical approach of the scientist with the sensibility of the artist. A book devoted simply to examples of visual tasks drawn from industry

and common experience, well illustrated with plates like the excellent though not numerous ones in Dr. Norden's book, and with commentaries by an author having both scientific and artistic ability, would be most welcome.

Finally, it is not out of place to say that one looks forward to the day when the attractiveness of the binding of a book such as the one here reviewed can be matched by the quality of the paper available for the text.

J. S. PRESTON.

Theoretical Structural Metallurgy, by A. H. COTTRELL. Pp. viii + 256. (E. Arnold & Co., 1948.) 21s.

The rapid progress of the physics and mechanics of solids in recent years has placed the majority of metallurgists in a difficult position: with the slender fundamental knowledge dispensed in most University metallurgy degree courses (Dr. Cottrell's University, Birmingham, is a praiseworthy exception) they can hardly follow recent scientific developments in their own field, let alone take an active part in them. Most of the pioneers in the science of metals have been physicists, chemists, or engineers by training; the activity of the professional metallurgist is usually confined to the application of available scientific results to particular metals and alloys, unless he is capable of acquiring the necessary fundamental knowledge by home study. In this difficult situation the appearance of Hume-Rothery's brilliant non-mathematical *Atomic Theory for Students of Metallurgy* in 1946 was an event of great importance, and Dr. Cottrell's new book represents a further welcome addition to the means by which the metallurgist can get acquainted with the modern aspects of the science of metals.

Dr. Cottrell's book falls into two parts of rather different character. The first six chapters give a good elementary account of the electron theory of metals, with a brief sketch of the Bohr theory and of the basic conceptions of wave mechanics; the remaining eight chapters deal with statistical thermodynamics, heterogeneous equilibria, thermodynamical properties of metals and alloy systems, order-disorder transformations, diffusion, and the kinetics of phase changes. These eight chapters treat their subject on a University science course standard; in fact, the amount of mathematics used is sometimes above the minimum necessary for the purpose.

Physicists may question whether a useful purpose is served by a mainly descriptive treatment of a mathematical subject such as is the electron theory of metals. In the reviewer's opinion the answer is definitely in the affirmative. A recent text-book entitled *Modern Metallurgy for Engineers* (New York: Pitman, 1941) gives a list of references to literature on metals, with brief commentaries on each item, and here Mott and Jones' book receives the following remark: "For enthusiasts on quantum mechanics. A few engineers may be interested in the mental calisthenics". Since the author of this revealing utterance is an influential metallurgist, and since the future of metallurgical education depends very much on influential metallurgists, little progress can be expected before these are convinced, by means of clear elementary reviews, that the physics of metals is no mere mental calisthenics unworthy of a he-metallurgist.

No doubt many metallurgists will take advantage of Dr. Cottrell's excellent book, and a new edition may have to be printed in due course. This would give an opportunity to increase the accuracy of expression in many passages which, although usually correct from a legalistic point of view, appear likely to be misunderstood by a beginner. One of the first examples of this is found on page 5, where the uncertainty principle might seem to have preceded quantum mechanics, in which "it has become necessary, however, to specify four quantum numbers instead of the single one used in the original formulation of the Bohr theory".

On page 34 the law of rational intercepts is thought to govern the positions, not of the natural crystal faces, but of lattice planes (for which the statement of the law would be partly trivial, partly—in its emphasis on *small* integers—wrong).

On page 43 we read: "There is some evidence, particularly from the study of crystals by x-ray diffraction, suggesting that a real crystal is not of perfectly uniform orientation, but is composed of a mosaic of small crystals, or crystallites." This seemed a possibility until 1934, when Renninger, using the double-crystal spectrometer, found that a synthetic NaCl crystal was ideally perfect in the sense of the Darwin-Ewald theory; recently Guinier,

by means of another x-ray method, came to a substantially identical conclusion for recrystallized aluminium. Thus, a "mosaic" imperfection is characteristic of a *bad* crystal, not of a *real* crystal; the early x-ray workers found most crystals imperfect because they did not know how to obtain perfect ones.

It is a pity that the last chapter, "Phase precipitation by nucleation and growth", does not include strain transformations (martensitic transformations), which are of the very greatest fundamental and practical importance in metallurgy. In this chapter Widmanstätten structures are attributed to oriented nucleation and growth governed by the condition of minimum interface energy. That the typical Widmanstätten pattern does not arise by such a process can be recognized from the very frequent occurrence of lamellae penetrating one another; the absence of isothermal growth, the reversibility of some strain transformations (e.g. the transformation of metastable β -brass by cooling), and many other phenomena show sufficiently that there can be no question of an explanation on the basis of oriented growth. Readers of this chapter will do well to follow it up by consulting Chapter XXII in Barrett's *Structure of Metals*, where a balanced view of the subject is given.

These remarks, however, should not obscure the fact that Dr. Cottrell's book is a most useful contribution to metallurgical literature; it deserves to be present in the library of every metallurgist, and it would certainly have deserved a more attractive paper and binding.

E. ROWAN.

Paramagnetic Relaxation, by C. J. GORTER. Pp. vii+127. (Amsterdam: Elsevier Publishing Co., 1947.) 12s.

This monograph, by the Professor of Experimental Physics in the University of Leyden, was written during the last winter of the German occupation of the Netherlands, when not only the absence of electricity, but even the risk of going into the streets, failed to put a stop to the academic work of the Physics Department of the University of Amsterdam. This little-known branch of magnetism, which deals with the magnetic analogue of dispersion and absorption in polar substances, is treated comprehensively from both the experimental and theoretical standpoints, and includes much unpublished work carried out in Holland during the war.

After an introductory chapter surveying the background of the work, the experimental methods, calling for magnetic susceptibility measurements at high frequencies, are reviewed.

The cogent features of the different methods and their results are discussed critically in the light of the new viewpoints, emphasis being placed on the various problems, both solved and unsolved, connected with adiabatic demagnetization and the theory of the crystalline state. The work constitutes a remarkable achievement under the most difficult conditions, and can be recommended to those seriously interested in this branch of paramagnetism.

W. S.

Vibration and Sound, by P. M. MORSE. Second Edition. Pp. xx+468. (New York and London: McGraw-Hill, 1948.) 33s.

The first edition of this book earned its place among the standard theoretical text-books on sound. In this, the second, edition the author has taken advantage of war-time developments in applied acoustics—to which he himself contributed not a little—to add material, particularly in the subjects of radiation, diffraction and transient phenomena. The latter especially is of great value in the study of musical instruments and auditorium acoustics. One is pleased to observe that sound is not treated as a watertight compartment in the vessel of physics, treatments being taken bodily and adapted from the theory of atomic radiation and of waveguides, for example.

Not the least valuable part of the text are the frequent thought-provoking problems to put the student on his mettle—he will not find the going easy. Operational calculus is employed in certain sections. However, with some judicious skipping, indicated by the author, the tyro is brought up gently from fundamental principles. Having thus scanned the field, it will be surprising if he does not start afresh, with his appetite whetted for a more detailed survey.

E. G. P.

Techniques Générales du Laboratoire de Physique. Vol. 1, edited by J. SURUGUE. Pp. 433. (Centre de Documentation du Centre National de la Recherche Scientifique, Paris.) 25s. (1,000 fr.) bound, 22s. 6d. (900 fr.) paper covers.

There are nine chapters in this book on laboratory methods. The opening chapter deals with principles of construction and is mainly on the kinematics of apparatus, though it also treats the mechanical properties of the commoner materials of construction. The general editor contributes a valuable chapter on vacuum technique, and others are on glass blowing, production of high temperatures, optical technique, light sources and filters, photoelectric cells, recording mechanisms and electrical apparatus.

A great deal of information is given in compressed form, and the book will be of interest to many laboratory workers. From the point of view of readers in this country, it has the incidental interest of teaching us many terms in French which we should find difficult to learn in any other way.

J. H. A.

Ishihara Tests for Colour Blindness, by SHINOBU ISHIHARA. Reprinted (1948) by H. K. Lewis & Co., Ltd. 50s.

Among the different types of colour vision test, the confusion charts are generally regarded as the most convenient as a first test. These charts consist of a series of cards on which a symbol such as a letter or number is formed from a pattern of coloured dots against a differently coloured background. By the correct choice of colours, the numbers may be easily seen by a person with normal colour vision, but may be misread or may be invisible to a person with defective colour vision, since he may be unable to distinguish the colour of the symbol from that of the background.

A successful test not only depends on the correct choice of the confusion colours but also on the shape of the symbols, the size of the dots and so on, since these will affect the ease of recognition of the symbol. The accuracy of reproduction is also vitally important if consistent results are to be obtained from different copies of the same test. One of the most satisfactory of the confusion chart tests, and probably the most widely used, has been the Ishihara test, originating in Japan. During the war there was an acute shortage of this test, and an English edition was accordingly published by Messrs. H. K. Lewis in 1943 and reprinted in 1944. This edition was not quite identical in colouring with the Japanese edition, but in a report on comparative tests carried out in the United States, the English edition was found to be generally satisfactory (*J. Opt. Soc. Amer.*, 1943, 35, 268, 350, 481).

For some time both the English and Japanese editions have again been unobtainable, but Messrs. Lewis have now issued a third printing (1948) of the English edition. The printing of these charts presents the colour printer with a very difficult problem, but comparison between the present printing and that of 1943 shows a very close similarity. Some differences are, however, noticeable, such as a tendency for the colours to be slightly stronger in the new printing, although tests on a defective observer did not suggest that these differences would have any significant effect on the practical value of the charts.

An adequate assessment of the charts would require a lengthy investigation with both normal and defective observers, but the new printing is on the whole so very similar to its predecessors that there is little reason to doubt that it should be given the same high rating as before. We should like to congratulate the publishers on their enterprise in bringing out this reprint, and the printers on their skill in carrying out their difficult task.

The Physical Society has a special interest in this question, since the Report on Defective Colour Vision in Industry prepared by the Colour Group and published by the Society recommended the use of the Ishihara test as a general purpose test. At the time of publication of the Report, in 1946, it was somewhat unfortunate that the test was virtually unobtainable. It is to be hoped that the more extensive testing recommended in the Report both in schools and in industry may be proceeded with apace now that this new copy of the Ishihara test is available.

Since the term "colour-blindness" is now widely regarded as misleading, we should like to suggest that any future editions be given the title "Ishihara Tests for Colour Vision" or "Ishihara Tests for Defective Colour Vision", although such a change would presumably require the approval of the original publishers.

H. M. CARTWRIGHT.
W. D. WRIGHT.

Frequency Modulation-Volume I, edited by A. N. GOLDSMITH, A. F. VAN DYCK, R. S. BURNAP, E. T. DICKEY and G. M. K. BAKER. Pp. x+515. (*R.C.A. Review*, Radio Corporation of America, R.C.A. Laboratories Division, Princeton, 1948.) \$2.50.

The material of this volume comprises a symposium of 24 articles by various members of the R.C.A. organization, all of which, with one exception, have appeared during the period 1936-1947 in either the *R.C.A. Review*, the *Proceedings of the Institute of Radio Engineers*, or various organs of the U.S. radio technical press. They have been selected so as to cover broadly the main aspects of frequency modulation theory and technique, and are arranged according to their subject matter rather than in their chronological order of appearance. After a preliminary group of four papers on the general noise-reducing properties and frequency bandwidth requirements of frequency modulation, the articles become more detailed in nature and deal with such subjects as propagation, antennae, generation and detection of frequency-modulated waves, and their application to particular services such as facsimile.

In addition to the articles reproduced in full, each section is followed by a number of further articles in summary form, and at the end is a bibliography containing some 88 titles, all from authors connected with the R.C.A. organization.

The value of this book, which in spite of its title is not to be regarded as a comprehensive text, lies in the assembly into one volume of a number of specialist papers which were previously distributed throughout the literature.

D. G. REID.

Radio at Ultra-High Frequencies, Vol. II (1940-1947.) Edited by A. N. GOLDSMITH, A. F. VAN DYCK, R. S. BURNAP, E. T. DICKEY and G. M. K. BAKER. Pp. x+485. (*R.C.A. Review*, Radio Corporation of America, Princeton, 1948.) \$2.50.

Over the past two decades the Radio Corporation of America has published in the R.C.A. Technical Book Series selections of the more important contributions of their staff to the *R.C.A. Review*, to the *Proceedings of the Institute of Radio Engineers*, etc. The present book is the eighth volume of this series and the second on the general subject of radio, *Radio at Ultra-High Frequencies*, Volume I, having covered the period 1930-1939.

The papers in the present book cover rather more than is indicated by the title, and include much material which could be classified as V.H.F. and microwave frequency technique. The papers are given in seven different sections: antennas and transmission lines; propagation; reception; radio relays; microwaves; measurements and components; and navigational aids. All the more important papers are published in full, a few are given in abstract, and there are appendices giving a summary of all the papers appearing in Volume I, and a bibliography covering all the papers published by R.C.A. on U.H.F. from 1925 to 1947.

The papers given in full have been well chosen and include several important papers on aerial theory and design by G. H. Brown and N. E. Lindenblad and their collaborators. There is also a very good collection of papers on receivers, including D. O. North's paper on "The Absolute Sensitivity of Radio receivers", V. D. Landon's paper on "The Distribution of Amplitude with Time in Fluctuation Noise", as well as several valuable papers by E. W. Herold on "Signal-to-Noise Ratio of U.H.F. Receivers". Altogether the book may be said to contain a very representative set of papers indicative of many of the latest techniques in the field of U.H.F. radio.

Many of the recent advances in radio and electronics depend on the research and development work in the higher radio frequencies, and many scientists and engineers who have difficulty in gaining access to the original papers will find the collection of papers given in this book of real value as the primary source of the contribution of the Radio Corporation of America in the field of U.H.F. developments.

DENIS TAYLOR.

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ABSTRACTS FOR SECTION A

The Size-Variation of Resistivity for Mercury and Tin, by E. R. ANDREW.

ABSTRACT. Measurements have been made of the low temperature resistivity of mercury wires down to 6μ diameter and rolled tin foils down to 3μ thickness. A continuous increase of resistivity with decrease of diameter and thickness was found, and it is concluded that this was due to a shortening of the mean free path of the conduction electrons by inelastic collision with the boundary surfaces of the metal. The theory of this effect for a wire is examined; a rigorous theory for a foil already exists (Fuchs 1938). By comparing the experimental results with the theory, values of the product lp are found for both metals; (l is the mean free path and ρ the resistivity for the metal in bulk). These values of lp are in satisfactory agreement with those obtained from Pippard's measurements on the anomalous skin effect for the two metals.

Critical Field Measurements on Superconducting Tin Foils, by E. R. ANDREW.

ABSTRACT. The critical fields of superconducting tin foils have been determined from resistance measurements in a longitudinal magnetic field. Pomeranchuk's relation, $H_f = H_c(1 + \lambda'/d)$, between the foil critical field H_f and the foil thickness d was verified, and values of the length λ' were found as a function of temperature; at $0^\circ K$, the value of λ' was estimated to be 1.2×10^{-6} cm., rising rapidly close to the transition temperature. It is noticed that λ' is approximately twice the penetration depth λ for tin at all temperatures. Assuming the validity of Ginsburg's interpretation of λ' as the sum of λ and the surface energy parameter β , it is seen that λ and β are approximately equal.

On the Radiation from Transient Light Sources, by F. BOOTH.

ABSTRACT. A theoretical treatment is given of the problem of analysing the radiation from transient light sources in the form of clouds of incandescent particles. Recently a method of correlating this radiation with various physical parameters has been suggested by E. F. Caldin. In the present paper a critical examination of this method is made, and exact formulae derived for special models.

Expressions for the radiation emitted by a cloud of incandescent particles, all at the same temperature, are obtained for the following cases: (i) a uniform spherical distribution of equal, perfectly emitting and absorbing particles; (ii) a uniform distribution of particles which are not perfect absorbers, but in which (a) radiation is reflected specularly from the particle surface, and (b) the particles reflect light diffusely; (iii) a uniform distribution of particles in a thin spherical shell.

It is shown that the condition for the radiation from a cloud of black-body particles to be equal in intensity to that from a black body of the same size and shape is that $R^2 a \rho_0 \ll M$, where R is the radius of the cloud, a the particle radius, ρ_0 the particle density and M the total mass of the cloud. The cooling of clouds by radiation transfer is also examined theoretically.

The bearing of the results on Caldin's method is discussed, and more exact methods of analysing the cooling of this form of light source sketched.

On the Schumann-Runge O₂ Bands emitted at Atmospheric Pressure, by M. W. FEAST.

ABSTRACT. The Schumann-Runge bands of O₂, previously analysed in the region 3100-4200 Å. and photographed below 3100 Å. under small dispersion, with only a tentative analysis, have been obtained from 2000 Å. to 5000 Å. on sufficient dispersion for the vibrational analysis to be extended and for the rotational structure to be clearly resolved. Conditions for their emission are discussed and the probable process, involving dissociation followed by recombination, is outlined. On this basis the results obtained in discharges, ozonizers and high-voltage arcs are explained. Flory's suggestion of predissociation in the upper state is reviewed and the experimental evidence found to be against it. The conclusions reached are applied to considerations regarding the spectrum of the night sky.

The CN Tail Bands emitted by the Carbon Arc in Air, by M. W. FEAST.

ABSTRACT. Wavelengths and intensities of twenty-one CN tail bands, observed in the carbon arc spectrum, are listed and v' , v'' values assigned. Nine of the bands have been previously reported as occurring in the nitrogen afterglow excitation. The intensities of the tail bands are shown to be in accordance with the accepted potential curves for this system.

Ultra-Violet Bands of Na₂, by S. P. SINHA.

ABSTRACT. The ultra-violet bands of Na₂ between λ 3600 Å. and λ 3200 Å. have been photographed in absorption in the first order of a 21 ft. concave grating with a dispersion of about 1.3 Å/mm. and their vibrational analysis carried out. All the bands belong to a single system and can be represented by the equation

$$v = 29342 + 119.33 (u') - 0.53 (u')^2 - 159.23 (u'') + 0.726 (u'')^2 + 0.0027 (u'')^3,$$

where $u = v + \frac{1}{2}$.

The heat of dissociation for the upper state is calculated to be 6510 cm⁻². The bands are due to transition from the ground $^1\Sigma_u^+$ state to an excited state which is probably $^1\Sigma_u^+$ in character. The dissociation products for the upper state are either 3 ²S + 4 ²P or 3 ²S + 3 ²D atoms of sodium.

On the Equations of Motion of Crystal Dislocations, by F. C. FRANK.

ABSTRACT. It is shown that when a Burgers screw dislocation moves with velocity v it suffers a longitudinal contraction by the factor $(1 - v^2/c^2)^{1/2}$, where c is the velocity of transverse sound. The total energy of the moving dislocation is given by the formula $E = E_0(1 - v^2/c^2)^{1/2}$, where E_0 is the potential energy of the dislocation at rest. Taylor dislocations behave in a qualitatively similar manner, complicated by the fact that both longitudinal and transverse displacements and sound velocities are involved.